ALKALI DEPOSITS
# FOUND IN BIOMASS POWER PLANTS

A Preliminary Investigation of Their Extent and Nature

A Joint Effort

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- ***University of California at***
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- ***National Renewable***
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- ***Foster Wheeler***
  Development Corp.

- ***U.S. Bureau of Mines***

Alkali Deposits

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A Preliminary Investigation of Their Extent and Nature

NREL Subcontract TZ-2-11226-1

SUMMARY REPORT

for

NATIONAL RENEWABLE ENERGY LABORATORY

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Foreword

These two volumes constitute the complete public record of a landmark laboratory and field study of the formation of alkali deposits in boilers firing a variety of real-world biomass fuels. Volume I was published by Thomas R. Miles, Consulting Design Engineers in April of 1995. It presents a broad overview and summary of the main results of both laboratory and field work. Volume II continues the discussion of alkali deposition, giving in greater detail the work of all participants.

Each volume is available from the National Technical Information Service. A limited number of copies are available to active researchers and industry. Please contact Dr. Richard Bain at the National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, Colorado, 80401.

The performers of this work are pleased to acknowledge the industrial participants and the Office of Solar Energy Conversion, Solar Thermal and Biomass Power Division of the DOE for their financial support and for technical and in-kind contributions.

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EXECUTIVE SUMMARY

Alkali in the ash of annual crop biomass fuels creates serious fouling and slagging in conventional boilers. Even with the use of sorbents and other additives, power plants can only fire limited amounts of these fuels in combination with wood. The National Renewable Energy Laboratory (NREL), U. S. Department of Energy, and the biomass power industry carried out eight full-scale firing tests and several laboratory experiments to study the nature and occurrence of deposits with the goal of increasing the quantities of these biofuels that can be used. This report describes the results of the laboratory and power plant tests that included: tracking and analyzing fuels and deposits by various methods; recording operating conditions; and extensive laboratory testing.

Occurrence of Deposits

Sintered or fused deposits were found on grates and in agglomerates in fluidized beds. Potassium sulfates and chlorides were found condensed on upper furnace walls where it mixed with flyash. Convection tubes were coated with alkali chlorides, carbonates and sulfates mixed with silica, alumina and complex silicates from flyash or fluidized bed media.

Deposits were evaluated using elemental analysis, X-ray diffraction and other mineralogical techniques. These analyses have advanced the understanding of the role of minerals in the combustion of biomass, and their occurrence in biofuels. Deposits occur as a result of the boiler design, fuel properties and boiler operation. The limited furnace volume and high furnace exit gas temperatures of most biomass boilers promote slagging or deposits from those biofuels that contain significant amounts of potassium or sodium, sulfur, chlorine and silica. All annual growth, whether from urban tree trimmings, annual crops or their residues, or from energy crops, contains sufficient volatile alkali (0.34 kg/GJ or 0.8 lb./MMBtu) to sufficiently lower the fusion temperature of the ash so that it melts in combustion, or the elements vaporize and condense on boiler tubes and refractories.

Deposits observed in this project are consistent with all known mechanisms for deposit formation: particle impaction, condensation, thermophoresis and chemical reaction. Particle impaction was the dominant mechanism, especially on cross flow convection tubes, followed by condensation on waterwalls and chemical reaction. Analysis by scanning electron microscopy (SEM) showed that compounds containing potassium, sulfur and chlorine were the principal bonding agents in most deposits and were usually associated with fuel blends containing annual growth materials such as agricultural crops and residues. Most deposits occur during post-combustion and cannot be predicted solely by analysis of the fuel composition.

Fuel and Deposit Analyses

More than 30 methods of analysis were identified for fuel characterization. Fuel sampling at biomass plants typically does not include enough information to evaluate potential sources of deposits. Routine fuel characterization should include: proximate analysis, ultimate analysis, heating value, chlorine, a direct measure of oxygen and elemental ash analysis. Samples should be ashed at 600° C to minimize the loss of volatile alkali. Microwave digestion in acids followed by atomic adsorption best accounted for fuel elemental composition. A successive leaching method called chemical fractionation was used to determine the reactivity of inorganic constituents in biomass fuels as measured by their solubility in water and acids (1 M ammonium acetate, and 1 M HCl).

Several techniques were used to analyze deposits. Scanning electron microscopy (SEM) helped to determine the composition and mineralogy of deposits. DTA (differential thermal analysis) and TGA (thermogravimetric analysis) were used to evaluate volatilization and fusion of ash constituents. Ash fusion temperatures using the pyrometric cone tests were of little value in predicting deposits, the alkali having been lost during ashing and calcining.

Pilot scale combustor simulations demonstrated deposit formation on combustor refractory and on heat transfer surfaces, confirming mechanisms observed in the field. Alkali volatilization, condensation and enrichment on flyash and in deposits were observed in the Sandia Multi-Fuel Combustor (MFC).

Boiler Design and Operation

Conventionally designed boilers are not suitable for burning high alkali fuels. Special boiler designs with low furnace exit gas temperatures, <1500° F, are required for annual crops or residues, including grasses and straws. Designs should include: adequate waterwall surface area or parallel heat exchange surfaces, and combustion air control to control gas temperatures, grates suitable for removing large quantities of ash, and sootblowing to clean tenacious deposits.

Limestone was the principal additive used in test boilers to maintain bed fluidization. While limestone improved operation the calcium appears as a constituent of deposits on convection surfaces (as $CaCO_3$, $CaSO_4$) and may reduce but does not prevent deposition. High alumina sand also reduced agglomeration in a circulating fluidized bed (CFB) but did not change the composition of deposits on the superheater tubes.

Gasification at low temperatures, <1400° F, with additives, may be necessary to inhibit alkali volatilization in order to burn large quantities of these biofuels. A review of straw experiences in Europe shows some success with straw pyrolysis. Additional research is needed.

Fouling and Slagging Indicators

Several methods were tested for anticipating slagging or fouling based on fuel composition. These included: concentration of alkali, water soluble alkali, tendency to form sulfates or chlorides, and direct observation on heating. Fuel elemental composition and the concentration of alkali, sulfur, chlorine and silica in the fuels appear to be the best indicators of the tendency of fuels to slag. Project data should be used to develop practical algorithms for industry. Observations of fuel samples heated to sticky temperatures during ashing showed differences between wood and agricultural residues but did not clearly identify problem fuels.

Project Participants and Reporting

Seven power plant sponsors joined the project representing nine biomass power plants: Delano Energy Company, Inc., Woodland Biomass Power Ltd., and Mendota Biomass Power, Inc., (representing Thermo Electron Energy Systems); Hydra-Co Operations; Sithe Energies, Inc.; Wheelabrator Environmental Systems, Inc.; and Elkraft Power Company, Ltd. (Denmark). Electric Power Research Institute, Foster Wheeler Development Corporation and the National Bioenergy Industries Association (formerly National Wood Energy Association) also contributed to the investigation.

The Bureau of Mines Research Laboratory in Albany, Oregon provided X-ray diffraction (XRD), scanning electron microscopy (SEM) and mineralogical analysis courtesy of Larry Oden. Sandia National Laboratories contributed pilot scale combustion tests and analyzed fuels and deposits as part of a parallel NREL project conducted by Larry Baxter. Bryan Jenkins, professor of Biological and Agricultural Engineering, participated through the courtesy of the University of California, Davis.

Results of the project were reported in presentations to nine conferences and will be published in forthcoming journals. Four project meetings were held with participants at Sandia National Laboratories. The suite of fuels and fuel samples developed during the tests were archived at Hazen Laboratories and were used in independent investigations by NREL and by Richard Bryers at Foster Wheeler Development Corporation. The conclusions from the project have changed the way participants evaluate deposits, and the way they buy and prepare fuels. Project data helped in the startup of a new biomass power plant in Florida. Through more than twenty five inquiries from biomass plants around the country it has been possible to assist other interested parties including: an industrial boiler manufacturer in the northeast, a power plant boiler manufacturer, other power plants, including a 20 MW power plant in New York and a plant cofiring wood and refuse derived fuel, many of the state and regional biomass energy agencies, and developers of short rotation woody crops and non-wood crops for fuel.

Future Work

Tube erosion and corrosion associated with deposits are of prime concern to industry participants. Development of a computer algorithm for predicting deposit formation combining information about fuels, deposits, boiler design and boiler operation would be useful. Further fuel characterization is needed. Deposit properties such as reflectivity, emissivity, porosity and tenacity also need to be characterized. Several other pilot and operational projects are suggested.

Recommendations

In summary and in answer to questions from the biomass fueled plant operators concerning how to proceed regarding alkali and deposits, the following steps are recommended:

1) Collect representative samples of all the fuels being used and those being considered.

2) Have a laboratory experienced in analyzing biomass fuels analyze the samples for proximate, ultimate, total chlorine, and elemental ash. See a typical analytical request form in Appendix B for methods recommended.

3) Either have the laboratory calculate the concentration of alkali and sulfur (lb. alkali/MMBtu or kg/GJ, Dry Basis) or calculate it from the analysis.

4) Compare the level of alkali in the fuel with other plant experiences burning similar fuels.

5) Strive to purchase fuels with alkali levels of 0.4 lb./MMBtu (0.17 kg/GJ) or less; or blend fuels to this maximum level, recognizing that blending may not prevent slagging or deposits from fuels with high alkali concentrations such as straw or nuts and shells. The tendency to form deposits or slag increases between 0.4 lb./MMBtu and 0.8 lb./MMBtu (0.17 to 0.34 kg/GJ), to definite fouling and possible slagging above those levels.

6) Prepare a schedule of blends by fuel types so that fuel entering the boiler has predictable deposit characteristics.

7) When fouling cannot be explained by the composition of the fuel or the furnace exit gas temperatures, examination of the deposits by SEM by an experienced laboratory can identify constituents that contribute to fouling.

ALKALI DEPOSITS FOUND IN BIOMASS POWER PLANTS

The Summary Report of a Preliminary
Investigation of the Causes and Mechanisms
of Boiler Deposits from Biomass Fuels

Sponsored and Implemented through the Cooperation
of Industry, Government and Academia
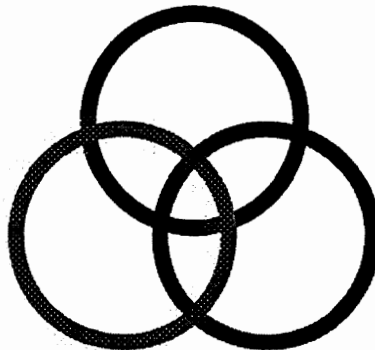
ALKALI DEPOSITS FOUND IN BIOMASS POWER PLANTS

1. INTRODUCTION

The demand for alternative sources of fuel increased as the biomass power industry expanded in the U.S. during the 1980s. When the new biomass power plants contracted to burn substantial quantities of crop residues with their wood and urban wood fuels, they experienced fouling of convection passes and severe deposits on grates and in fluidized beds, despite the use of sorbents and other measures. These problem fuels characteristically contain high levels of potassium and other alkalis and alkaline earth metals which vaporize or react with other elements as they pass through the boiler, partially condensing to form sticky deposits on metal and refractory surfaces. As a result, power plants cannot use these slagging fuels to the extent stipulated in their original operating permits. Instead, they rely primarily on industrial and urban wood wastes that contain less ash and alkali. Increased competition for fuels and problems of solid waste disposal again make low quality fuels important potential resources for power plants. Recognizing this, the National Renewable Energy Laboratory (NREL) initiated a joint study with industry to identify the occurrence of alkali deposits and to suggest possible solutions so that greater quantities could be fired in power boilers. NREL funding for the project was fully matched by nine industry co-sponsors. (Miles, et al., 1994)

The Project

The project consisted of fuel sampling, field test firing, analysis of fuels and deposits, and database development. The biomass electric power industries contributed their experience and made their facilities available for testing. An advisory team of experts worked with the industries to identify problems, to assess the suitability of current solutions and to suggest future directions.

The project included:
    Review of the literature and power plant experience.
    Eight full-scale firing tests in five power plants.
    Field collection, tracking, and analyses of fuels and deposits in each boiler configuration.
    Sampling and extensive analyses of more than 26 biomass fuels using as many as five different methods.
    Laboratory combustion tests in the Sandia Multi-Fuel Combustor (MFC).
    Evaluation by participating operating personnel, scientists and engineers.

Protocols were developed for fuel and deposit sampling and analysis, including methods such as chemical fractionation that had not previously been used with biomass. Boiler operation was observed when firing high and low alkali fuels. Boiler conditions were simulated in the pilot scale Multi-Fuel Combustor (MFC) for eleven fuels from the field tests. (Baxter, et al., 1993; Jenkins, et al., 1994; Baxter, 1993-1994)

Analytical Approach

Investigations of biofuel deposits often attempt to correlate the fusion temperature of the ash as determined in the laboratory with fouling or slagging in the furnace. Investigators usually interpret results by applying coefficients obtained empirically from coal combustion. This was the common theme of a literature search with hundreds of citations (Rose, 1993). Power plant experience shows that this approach does not adequately predict or explain fouling or slagging from biofuels. Mineral composition in biomass differs from coal, especially in the amount of potassium, calcium and chlorine. Furnace operating temperatures and combustion conditions also differ, resulting in deposits that have different characteristics and occurrences. This project traced the transformations of inorganics through the boiler by using analytical techniques that more accurately characterize deposits in order to identify how they form (Baxter, 1993).

Project Participants

In August of 1992 a grant was provided by NREL with the hope of enlisting contributing sponsors from industry. Eventually seven power plant sponsors (one from Denmark) joined the project representing more than nine biomass power plants: Delano Energy Company, Inc., Woodland Biomass Power, Ltd., and Mendota Biomass Power of Thermo Electron Energy Systems; Hydra-Co Operations; Sithe Energies; Wheelabrator Environmental Systems, Inc.; and Elkraft Power Company, Ltd., Denmark. Electric Power Research Institute, Foster Wheeler Corporation and the National Bioenergy Industries Association (formerly National Wood Energy Association) also contributed to the investigation.

Thomas R. Miles, P.E., provided a design engineer's perspective and with Thomas R. Miles, Jr. coordinated the project, locating industry and other expert participants and arranging meetings and tests at laboratories and operating plants.

Dr. Larry Baxter, Combustion Research Facility, Sandia National Laboratories in Livermore, California, contributed his experience from coal research, conducted Multi-Fuel Combustor tests, chemical fractionation and deposit interpretation as part of a parallel NREL project (Baxter et al., 1993, Baxter, 1994, 1995). Mr. Richard Bryers, *emeritus*, Foster Wheeler Development Corporation, contributed analysis and interpretation of fuels and deposits including low temperature ashing and DTA analysis (Bryers, 1993, 1994). Dr. Bryan Jenkins, Biological and Agricultural Engineering Department of the University of California at Davis, contributed his long experience with biofuels, supervised a literature review, coordinated field tests, and analysis and interpretation of deposits in the field and in the laboratory (Jenkins, et al., 1994). Mike Jones, Sithe Industries, was the project field coordinator for plant tests. Dr. Laurance Oden, US Bureau of Mines Research Laboratory at Albany, Oregon, provided X-ray diffraction (XRD), scanning electron microscopy (SEM) and mineralogical analysis (Oden 1993, 1994). Eric Winther, Elkraft Power, Ltd., contributed experience with firing straw in Denmark and hosted site visits by T.R. Miles, Jr. (Miles, Jr., 1993). He provided Danish reports on deposits and corrosion (Jansen, 1989).

Other advisors to the project who contributed their experiences with fouling in coal combustion included George Wiltsee, Appel Consultants; Jerrold Radway, EnerChem, Inc.; and Al Duzy. Technical cooperation was provided by Richard Bain, Ralph Overend and Tom Milne at NREL. Thus the project included a consortium of industry, science and engineering.

Project Reporting

Results and progress of the project were reported to the participants in four meetings at Sandia Laboratories and through interim reports. The Deposit Bulletin was issued from time to time and comprehensive progress reports, analyses and tests were provided to attendees at the meetings October 19, 1992, May 19 and November 30, 1993, and April 4, 1994. Nine presentations about the project were made to technical audiences. These papers have stimulated many phone calls from the US and abroad for more information about fuels and slagging.

The detailed descriptions of tests and their interpretations are principally explained in these reports which are combined and summarized in the following sections. Section 2 describes the test boilers and industry experience with deposits. Section 3 describes the methods and results of fuel analyses. Standard methods are cited with examples of fuels analyzed, fuel supply, preparation and variability, typical properties of biomass fuels affecting deposition, and the occurrence of important elements as determined by chemical fractionation and ash fusion methods. Section 4 summarizes laboratory and field studies of deposits from the combustion of straw and grass, shells, hulls and pits, and commercial wood and shell blends. Section 5 summarizes the mechanisms of deposition observed during the investigation and reviews slagging or fouling indicators. The project resulted in research strategies and conclusions listed in Sections 6 and 7. Many of the fuel and deposit analyses developed during the investigation may be found in Appendices C and D and in the reports listed in the References.

2. BOILERS

Field tests were conducted at host power plants operated by industrial sponsors in California and Denmark. Plants ranged in capacity from 5 MWe to 25 MWe employing state-of-the-art boilers developed for biomass since 1980. These included conventional traveling grates with spreader stokers and dedicated folded boiler designs, fluidized beds and circulating fluidized beds. Table 1 shows the size, capacity and fuels of the test boilers. They are shown schematically in Figures 1 and 4. These boilers were operated at similar bed temperatures and furnace exit gas temperatures from 850° C to 950° C (1560° F to 1750° F) with the exception of the straw fired stokers. The spreader stoker traveling grate (Grate-1) is the most common boiler design used for wood and biomass power.

The dedicated straw-fired cogeneration plants in Denmark (Grate-2, Grate-3) are special because they have greater waterwall areas and lower furnace exit gas temperatures of 760° C (1400° F) to produce principally low temperature steam. Three boilers that participated in the project were of the folded furnace design shown in Figure 2 (Grate-2, 3), similar to a design for waste-to-energy plants. Two of these were built in Denmark as first generation systems for combined heat and power where process steam is the principal product. The third plant, also in Europe, was built for a blend of wood and manure. These designs incorporate staged combustion, where one third of the combustion air is supplied through the grate so that fuel is burned at low temperatures and the rest is added above the grate for high temperature combustion in the gas phase. Furnace exit gas temperatures are kept low, 1400° F, with added surface area which tends to keep the deposits in the furnace instead of continuing into the convection passes.

Problems with deposits were not originally expected with biomass fuels so few of the furnaces tested included extensive sootblowers, slag screens or other devices for cleaning or removing sticky ash in their original designs.

Table 1 Boilers in the Alkali Deposit Investigation

Type		FBC-1 Fluidized Bed	CFB -1, 2 Circulating Fluidized Bed	CFB - 2 Circulating Fluidized Bed	CFB -3 Circulating Fluidized Bed	Grate-1 Traveling Grate+stoker	Grates 2-3 Straw Boilers
Gross Capacity	MWe	27	28	28	18	20	5-11.7
Steam flow	th⁻¹ (Kph⁻¹)	116 (255)	118 (260)	118 (260)	77 (170)	84 (185)	26-40 (57-88)
Steam Pressure	kPa (psi)	9308 (1350)	6240 (905)	6240 (905)	6206 (900)	6378 (925)	6701 (972)
Steam Temp °	°C (F)	513 (955)	454 (850)	482 (900)	482 (900)	421 (790)	450 (842)
Furnace Exit Temperature	°C (F)	960 (1760)	882 (1620)	882 (1620)	900 (1650)	850 (1560)	640-760 (1184-1400)
Fuel consumed	dry t/h	30	30	30	22	22	6-8
Fuels		urban wood ag prunings	wood, ag nuts, shells	urban wood ag	urban wood ag	urban wood straw	straw

Units: th-1, metric tonnes/hour (K Pound Steam per hour x 0.454
kPa = 6.895 x psi

Figure 1 Schematic Configurations of Test Boilers with Grates (Jenkins et al., 1994)

Grate-1
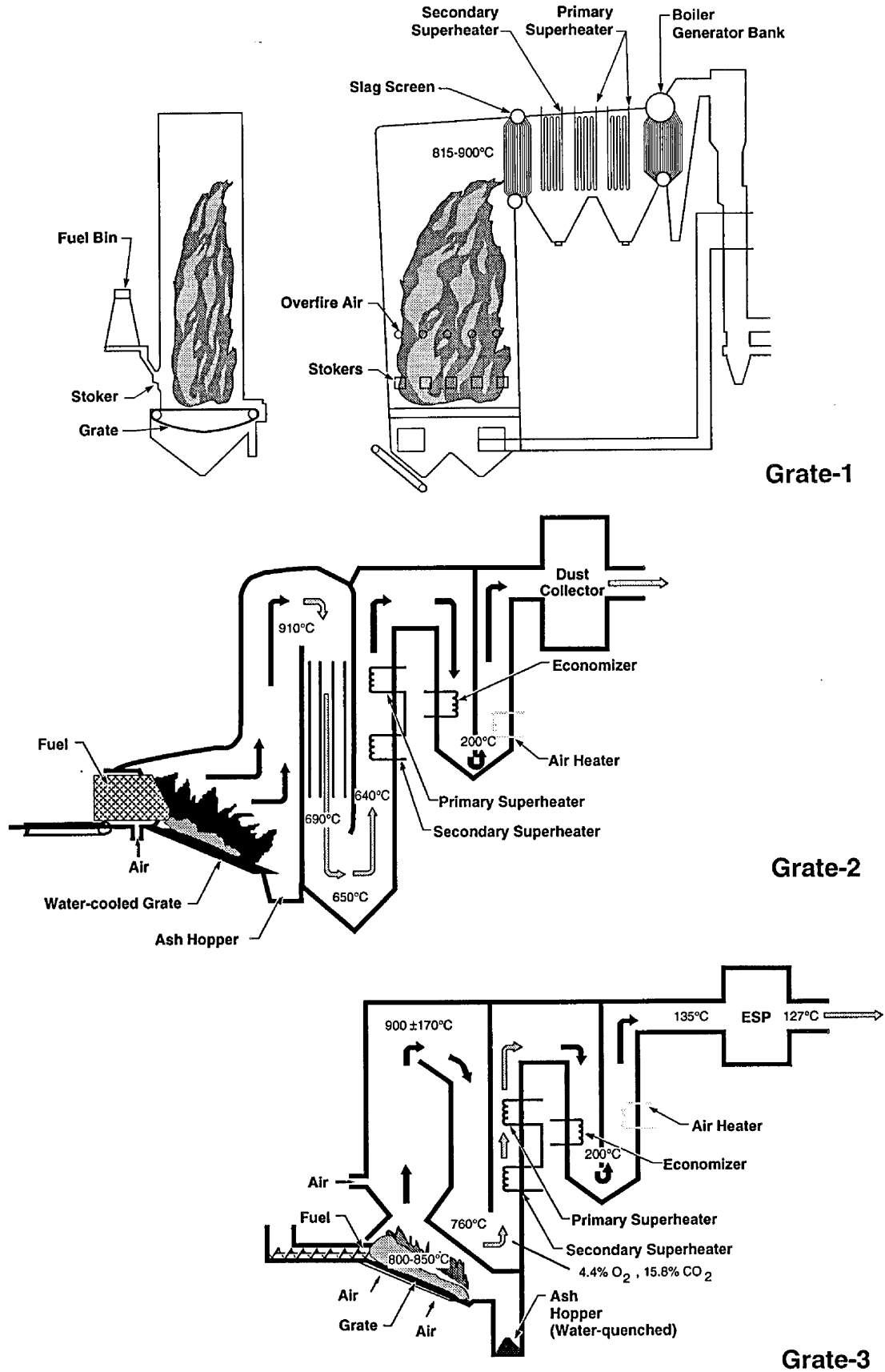
Grate-2

Grate-3

Figure 2 Grate-1. Spreader stoker with traveling grate, 20 MWe, Imperial, CA
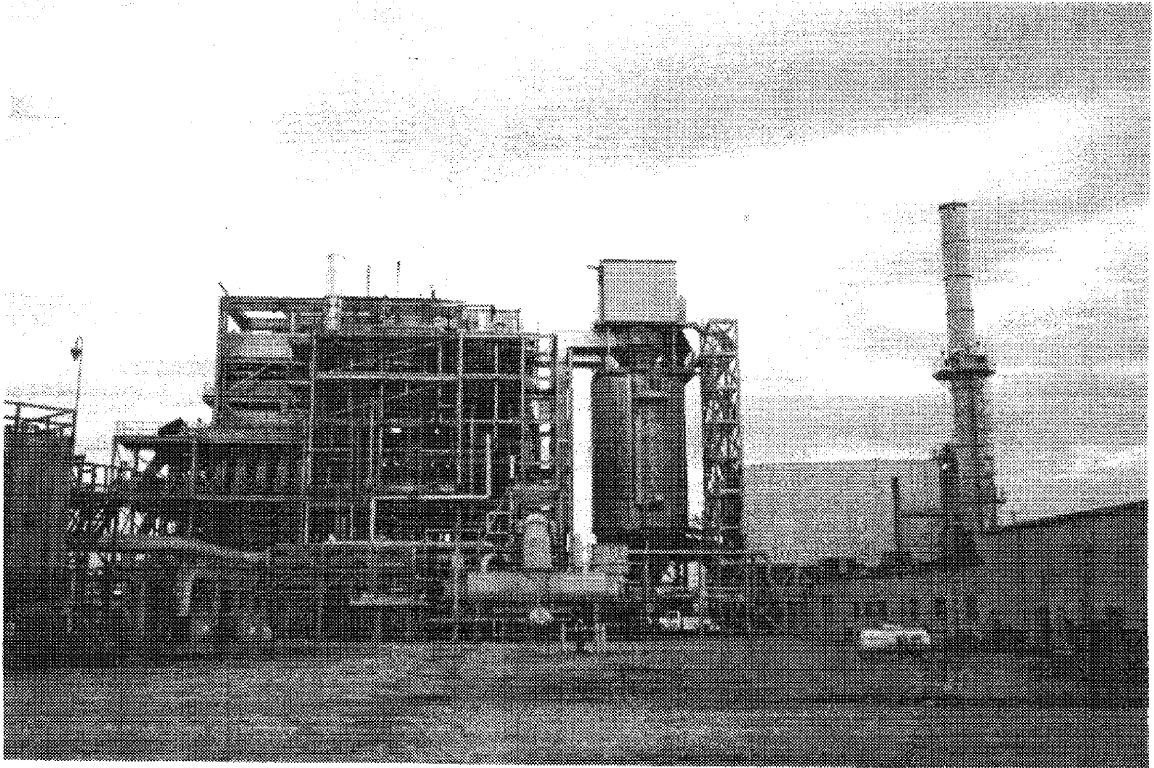
Figure 3 Grate-3 Straw fired moving grate CHP 5 MWe, Slagelse, Denmark
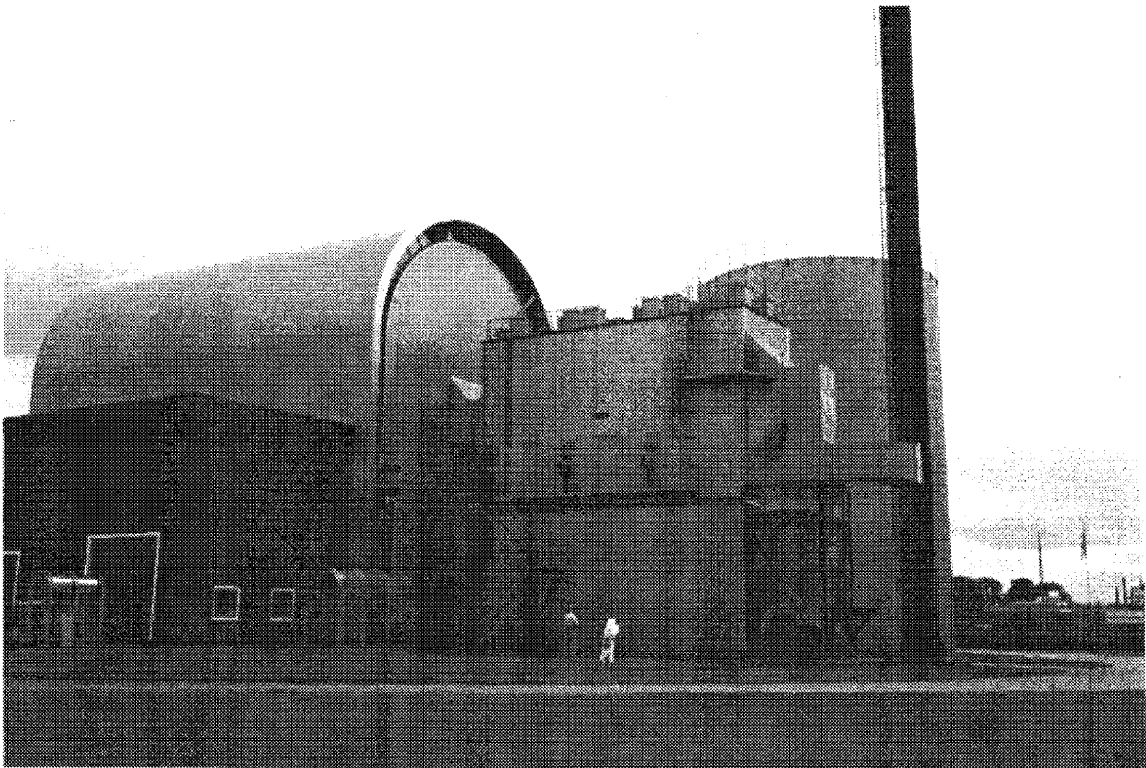
Figure 4 Schematic Configurations of Test Boilers with Fluidized Beds (Jenkins et al., 1994

FBC-1

CFB-1 and 2

Characteristic Superheater Deposit Profiles

CFB-3
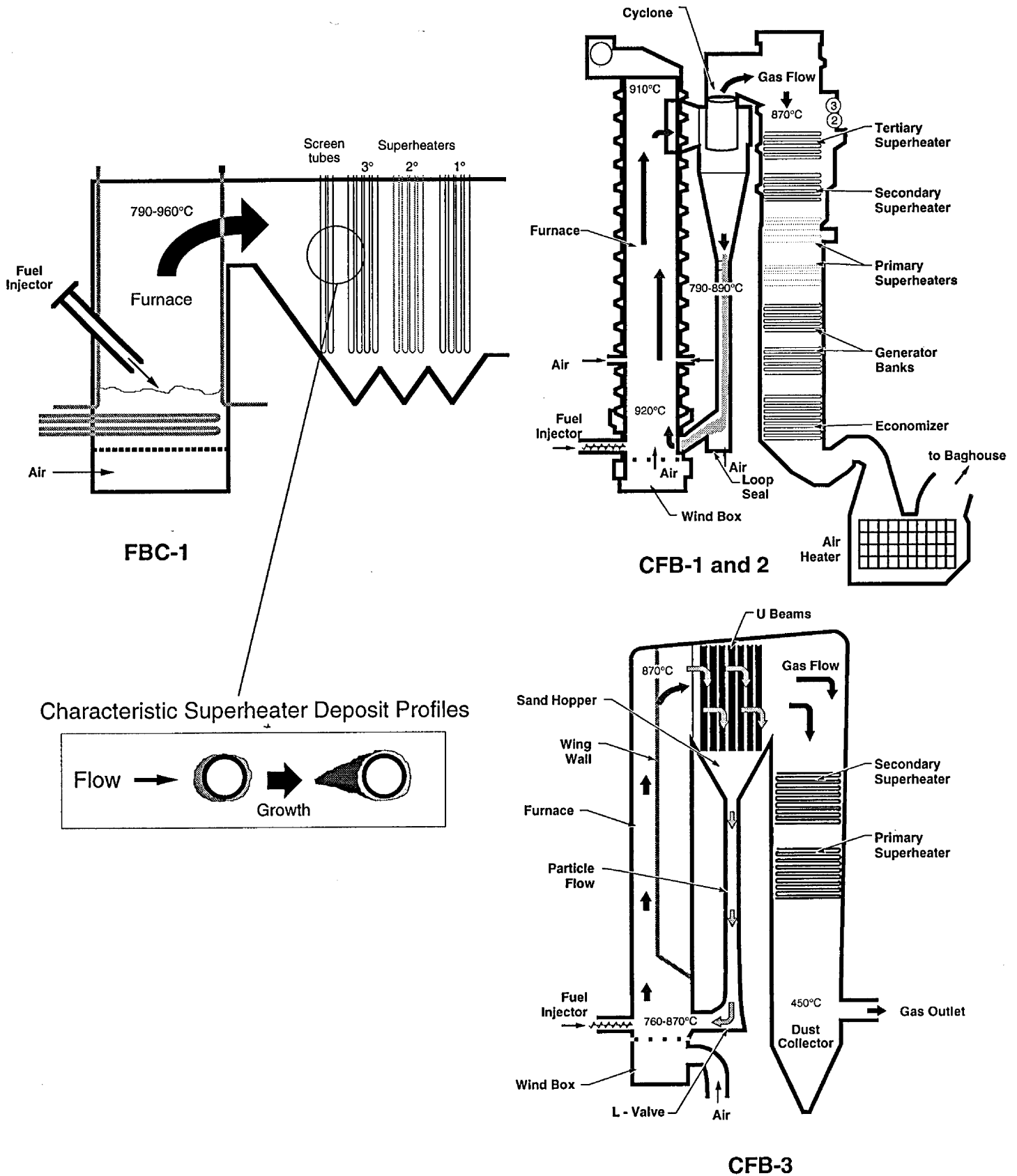
Figure 5 CFB-1 Circulating fluidized bed, 25 MWe, Woodland, CA
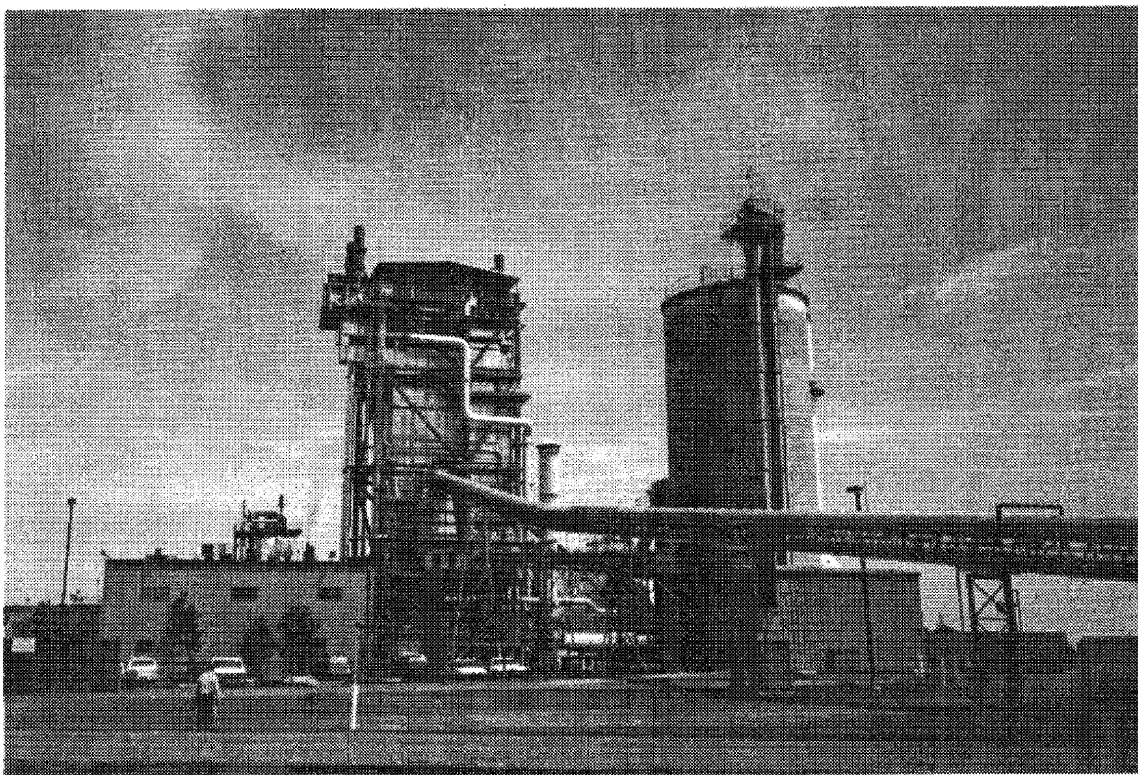
Figure 6 FBC-1 Bubbling Fluizided Bed, 25 MWe, Delano, CA
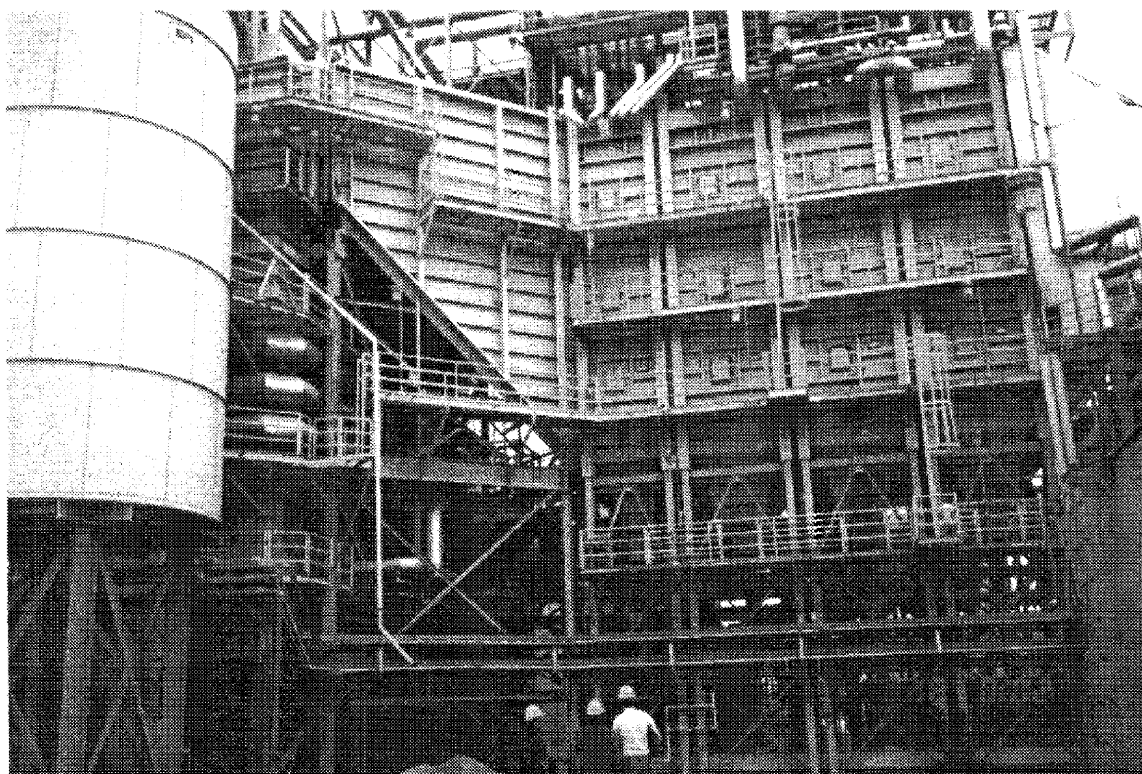
Survey of Deposits in Biomass Plants

In October 1992 several biomass plants were surveyed to determine the importance of alkali deposits to their operations. All of the final project participants responded, in addition to other biomass plants in California. The National Bioenergy Industries Association also surveyed their member plants and manufacturers. At that time the NBIA manufacturers and plants, mostly located in the East and Southeast, reported few deposit problems but anticipated future problems as fuel quality deteriorated. Since that inquiry several plants in that region have reported severe slagging, deposits and corrosion.

Participating biomass power plants included spreader stoker traveling grates, fluidized and circulating fluidized bed boilers as shown in Table 1 and Figures 1 to 6. Many of the plants have used a variety of techniques to prevent or remove deposits including fuel management, boiler control and cleaning, or additives, but without continued success. They cited benefits expected from reduced slagging, fouling or deposits as:
1. Reduced maintenance outages and costs,
2. Improved steam plant efficiency or capacity,
3. Extended or expanded fuel supply, and
4. Reduced corrosion.

Fireside problems reported were:
1. Ash removal problems,
2. Large deposits on refractory surfaces,
3. Deposits on refractory but not waterwalls,
4. Spalling, slagging, viscous slag,
5. Accumulation around air tuyeres and refractory,
6. Fuel feeder blockage from slag,
7. Fluidized bed media agglomeration,
8. Blockage of gas passages by deposits,
9. Fine fuels generate hot spots by after-burning, and
10. Erosion of transitions in gas ducts.

Convection pass fouling, erosion, and corrosion effects were described as:
1. High temperature bonded deposits in the superheater,
2. Bridging and blockage of convection passes,
3. Erosion of superheater tubes,
4. Loss or attenuation of steam capacity, and
5. Corrosion in the superheater, air heater, and economizer.

Plants reported using a variety of methods to prevent or remove deposits, including fuel management, boiler control, cleaning and additives. Fuel management techniques were:

1. Eliminate worst acting fuel components,
2. Dilute "dirty" fuels with clean fuels,
3. Schedule worst fuels prior to scheduled outages,
4. Ash chemical analysis,
5. Limit nuts and shells or suspected fuels in fuel mix to less than 5% to 10%, and
6. Screening to remove fines.

Boiler control included:
1. Operator training and sensitivity, and
2. Tune combustion controls to limit temperature excursions.

Cleaning and additives included:
1. Bed media blowdown, screening and reuse, inspection,
2. Sootblowing techniques and hydroblasting, and
3. Addition of limestone based on boiler condition.

The surveys and initial project meetings and site visits to participating plants resulted in several research questions that the investigation attempted to answer. Operators of existing biomass plants wanted to know:

1. How to fire up to 30% or 40% of alkali fuels,
2. How to identify slagging fuels,
3. What criteria to use to formulate fuel blends,
4. How to manage deposits without shutting down,
5. What additives could be used with specific fuels, especially straws,
6. What tube alloys and refractories to use,
7. Whether to screen or further process fuels on site,
8. What are the effects of chlorine, dirt or fines, and
9. What causes corrosion?

Many of these questions are answered by applying the mechanisms of deposition studied in this investigation to specific fuels and boilers.
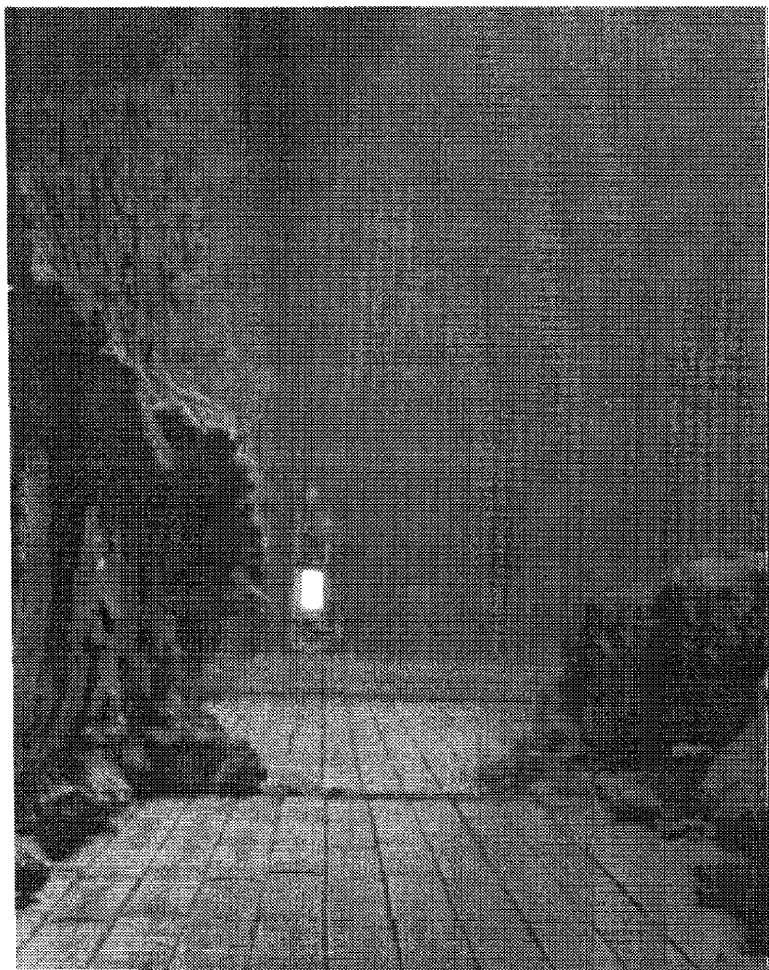
Figure 7 Slagging on wall after four days of burning a high percentage of Urban Tree Trimmings in Grate-1. Deposit that fell from wall is 3' high and 14' long. 4 days operation. (Hydraco 1992)

Figure 8   Grate-1.
Opposite view of deposit.
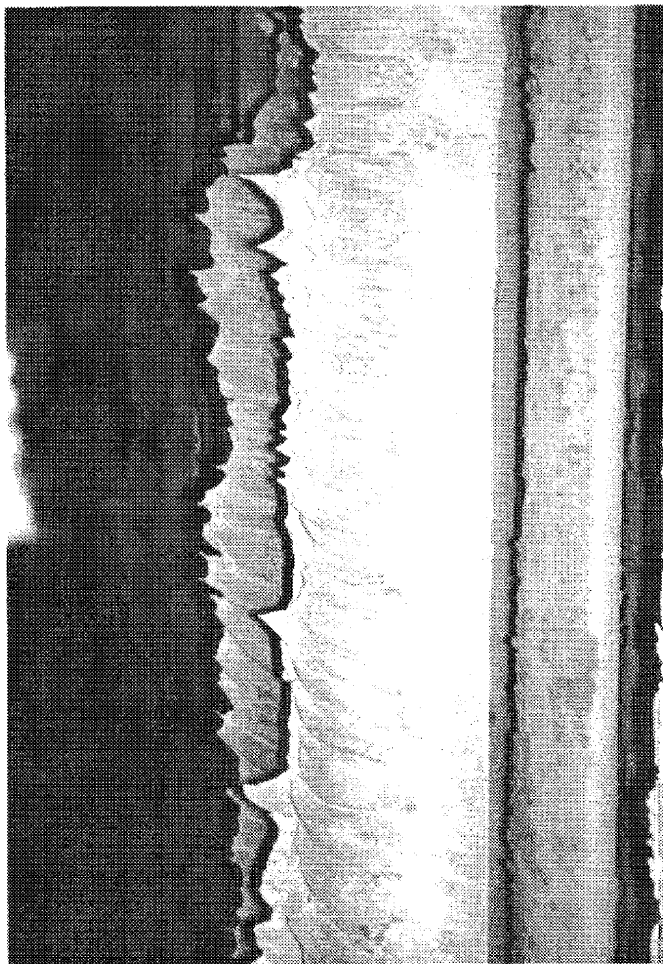
Figure 9 Tertiary Superheater Deposits from Wood-Ag Blend FBC-1 (Delano)

FLOW →
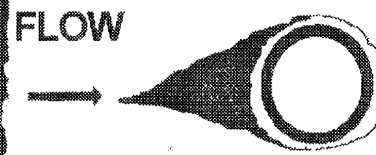
See Figure 4 for deposit location.

Figure 10 Superheater Deposits from Straw Fired Stoker Grate-2 (Haslev, 1993)
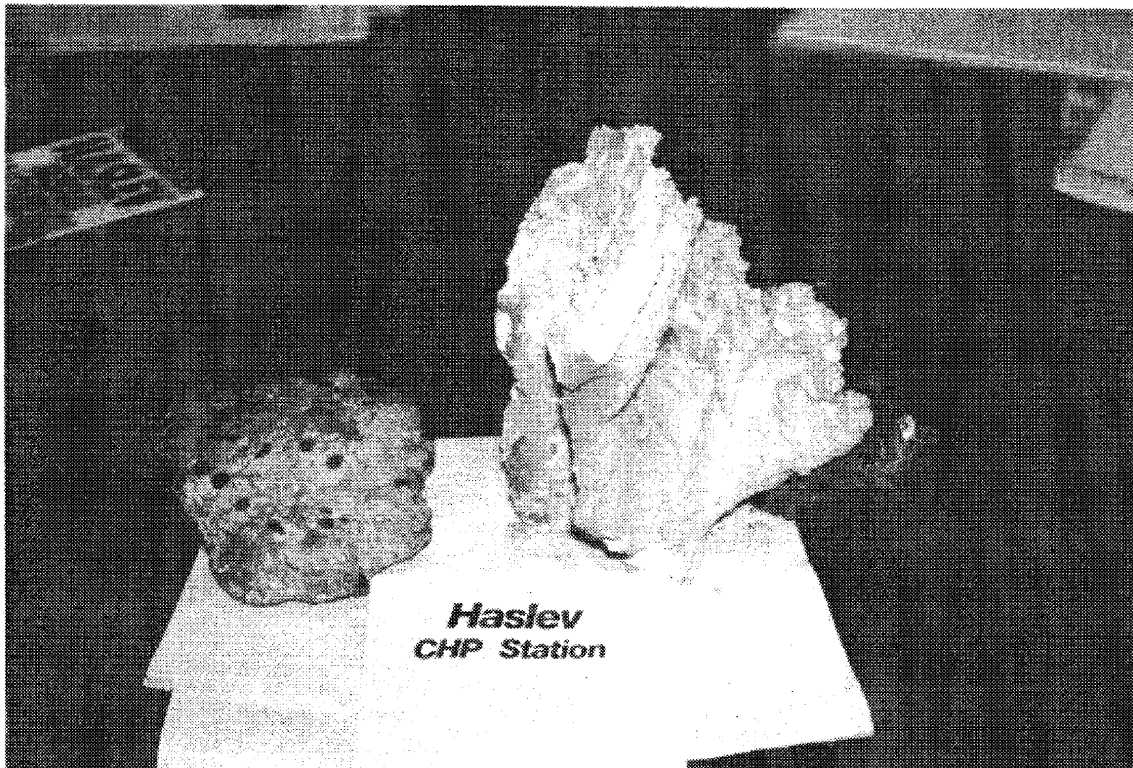
3. FUELS AND ANALYSES

One goal of the Alkali Deposit Investigation was to provide analytical data, slagging indices and other recommendations to aid in fuel selection or blending. Plants provided fuel analyses, records of fuel use, descriptions of their experiences with firing different biomass fuels, and they also recommended analytical laboratories. More than 26 different types of fuels and blends were analyzed. Fuel analyses were compiled into a database (Miles, et al., 1994). Selected fuels were also analyzed to determine which characteristics of the ash promote slagging or fouling. These tests included: alternative methods of elemental analysis; thermal and wet chemical methods to produce ash below volatilization temperatures; and, methods to determine the solubility of inorganics in the ash (Oden, 1993, Bryers, 1994). Samples were also provided to other alkali-related projects (French, et al.,1994).

The test plants associate slagging and deposits with a wide range of wood and agricultural fuels. Table 2 lists those fuels and shows the tests performed during this project. Typical analyses can be found in Appendix C. Wood and urban waste fuels include wood from the forest industry, forest residues, plantation wood, urban construction and demolition wastes, mixed waste paper, landscape prunings, and stumps and prunings from orchards. The power plants are evaluating willow, hybrid poplar and other woody biomass plantation crops for the future. Seasonally, they have available nuts, pits and hulls from fruit processing and grasses including wheat straw and rice straw. Other grasses such as switchgrass and miscanthus are being evaluated as future energy crops. Manures of interest to the test plants include chicken manure where rice hulls or wood are used as the bedding material.

Table 2 Tests Conducted on Biomass Power Plant Fuels

Wood and Urban Wood Wastes	Field	MFC	Lab
Mill wastes including bark	X		X
In-Forest Whole Tree Chips, pine, fir, hardwood			X
Plantation wood, whole tree chips: willow, poplar	X		X
Urban wood waste	X	X	X
Construction demolition and land clearing	X	X	X
Urban wood with landscape prunings	X		X
Mixed waste paper, urban		X	X
Orchard prunings, citrus	X		X
Almond prunings, stumps	X		X
Grape vine prunings			
Walnut wood, prunings			
Nut shells and hulls, pits			
Almond shells, hulls	X	X	X
Olive pits	X	X	X
Peach pits	X		
Pistachio shells	X		X
Prune or plum pits			
Walnuts and shells	X		X
Field crops: hulls, straws, stalks, fibers			
Alfalfa straw			X
Asparagus fern			X
Bana grass			X
Bermuda grass straw			X
Miscanthus			X
Rice hulls	X		X
Rice straw		X	X
Switchgrass		X	X
Wheat straw	X	X	X
Manure			
Chicken manure, or litter			X
Race track straw and manure	X		X

* Key to fuels testing:
F = field trials at industrial sites
M = laboratory combustor trials, Sandia Multi-Fuel Combustor
L = laboratory analyses
See Section 3 and Appendices B-D for test methods and results.

Fuel Supply, Preparation and Variability

The supply of biofuels is changing and the biomass industry may need to burn low quality fuels to survive in the future. The ability to burn significant quantities (30%-40%) of high alkali or low quality fuels should extend the fuel supply and thus result in economic and environmental benefits to the plants. Clean wood supplies have diminished since the existing plants were built. Several plants that were intended to burn agricultural residues have closed or shifted to wood wastes. Plants built to burn straw to offset open field burning, such as the Danish plants, have been struggling to burn straw economically.

Urban landscape prunings, hardwood whole tree chips, and agricultural and field crop residues including straws, nuts, shells and hulls were identified as the most problematic fuels. A variety of fireside and convection pass problems were reported. These fuels have been associated with the high levels of alkali. Plants burning these fuels have derived some formulas for blending, such as burning no more than 5% high alkali fuels, equal to 1 ton per 20 tons of blended fuel per hour. These formulated blends still result in significant cleaning costs, and operational problems. No plant has been able to burn higher rates at sustained levels without operating problems.

Ash and alkali levels for fuels recorded at the test plants were higher than reference values in the literature. They were at the upper range of the typical fuel "specifications" for biofuels, and higher than commonly used in wood fired boilers.

While fuels are identified here by type it should be noted that there is considerable variability within fuels that is created by fuel supply, preparation and processing as well as local conditions such as soil chemistry and rainfall. Fuel supply is influenced by economic local and seasonal factors. Fuel size, moisture, percentages of fines and foreign matter can influence furnace operation depending on the furnace design. The variability of fuels is illustrated in Figure 11 which records the blend of six different types of fuels fired during an eighteen week period in one of the test boilers (Jenkins, et al., 1994). While a plant may be able to maintain a uniform ash level with this kind of mix, the types and forms of inorganic elements in the ash change the susceptibility to slag formation or fouling.

Woodland Fuel Mix, Spring-Summer 1993

Legend:
- Eucalyptus
- Almond
- Coffee
- Mich Cal
- Pit Mix
- Pits
- Sawdust
- Shells
- Prunings
- Pine Dust
- White Pine
- WEYCO
- UWW
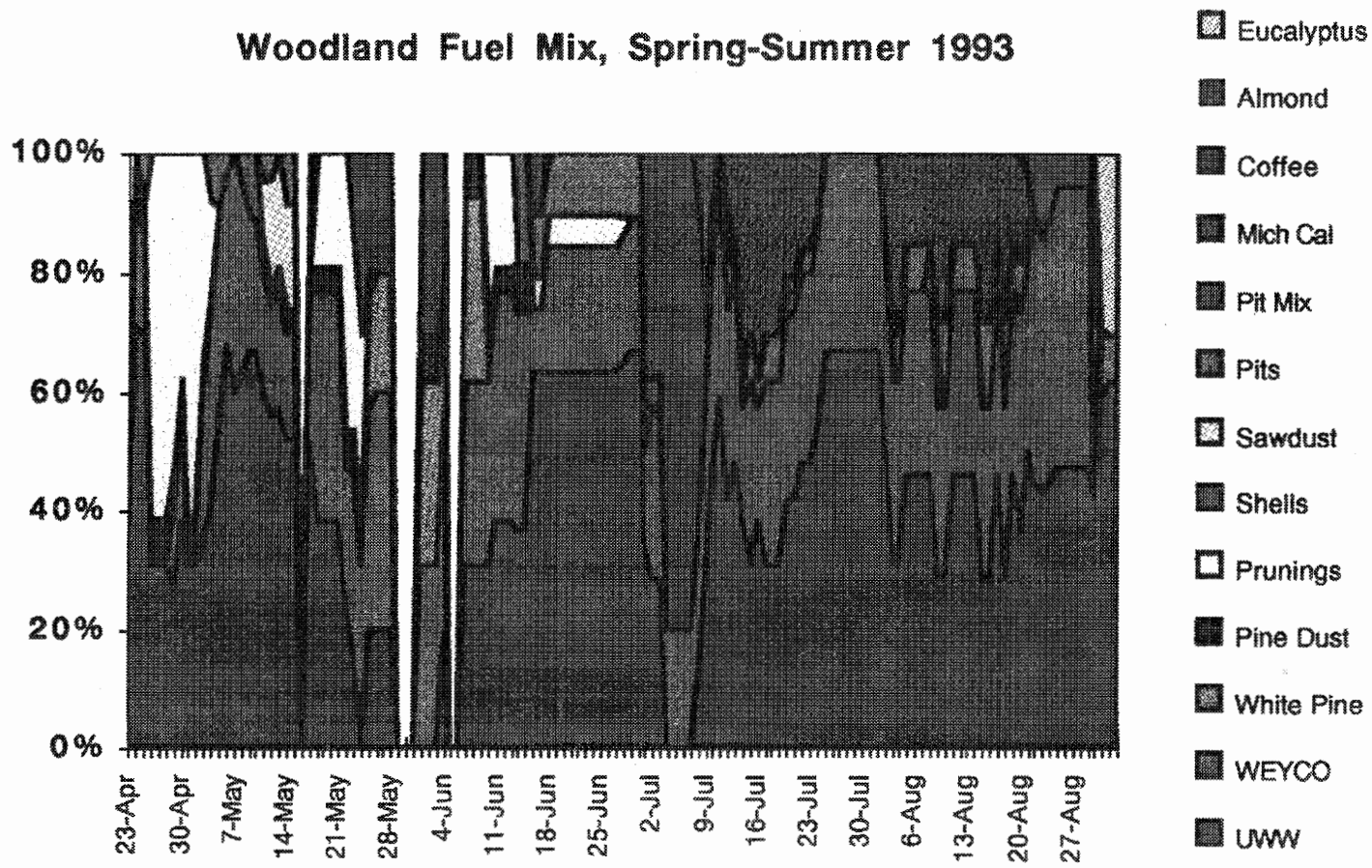
Figure 11 Variability of Fuel Mix Spring-Summer 1993

Fuel Characterization

Biomass plants usually sample fuels to assure compliance with contract specifications for moisture, ash and heating value but do not include elemental ash composition (McBurney, 1993). Potassium content in particular is important to indicate potential ash fusion or ash deposition through vaporization and condensation. Potassium is transformed during combustion and combines with other elements such as chlorine, sulfur and silica. Plant operation has improved, and slagging and fouling have been reduced where participating plants have systematically sampled and analyzed the alkali in fuels by methods used in this project, and correspondingly selected their fuels to reduce alkali input. The term "alkali" is used to describe the sum of potassium and sodium compounds, generically expressed as the oxides K_2O and Na_2O. The alkali earths, MgO and CaO, are also important in slagging and deposit formation, their very high fusion temperatures tending to inhibit the eutectic effect of alkalis - especially in fluidized beds.

More than thirty analytical methods were identified that could be used to characterize biomass for fuel (Jenkins, 1993, Appendix B). This project used the guidelines of the Biomass Boiler Test Procedure proposed by the Technical Association of the Pulp and Paper Industry (TAPPI) Steam and Power Committee to define sampling methods and procedures. TAPPI also specifies American Society of Testing and Materials (ASTM) methods of analysis for fuel size and ash composition (TAPPI, 1992). As a result of this project the methods shown in Table 3 are recommended for routine fuel characterization. A sample analytical request form is shown in Appendix B.1.

While several methods of fuel analysis are similar, some significant differences exist that can produce misleading results. Oxygen should be measured directly. Most laboratories calculate oxygen as the difference between the total sample mass and that of the other major elements. However, other elements such as chlorine may distort the oxygen value. Chlorine should be a normal part of fuel analysis because of its importance in alkali release. CO_2 should also be a part of any ash analysis and the ash should be prepared at temperatures not higher than 600° C.

Detailed analysis may be warranted where operational or environmental problems occur. These include the routine analysis plus chemical fractionation, as described below, trace elements and heavy metals, direct oxygen measurement, and thermogravimetric analysis. Ash fusibility (pyrometric cone test) is of limited value. Analysis of screened fines (<8mm) in dirty fuels indicates whether the whole fuel should be screened to avoid problems from high ash and alkali.

Table 3 Methods and Units for Fuel Characterization

Methods and Units for Fuel Characterization

	Biomass	Coal
Bulk density, lb./cf, kg/m3;	E 873	
Fuel size	E 323	
Calorific Value,		
BTU/lb., MJ/kg	D 2015 E 711	D 2015
Proximate composition		D 3172
Moisture	E 871	D 2013, D 3173
Ash	D 1102, E830	D 3174
Volatiles	E 872/E 897	D 3175
Fixed Carbon	By difference	By difference
Ultimate Analysis:		D 3176
C,H	E 777	D 3178
N	E 778	D 3179
S	E 775	D 4239, D 3177
Cl	E 776	D2361, AOAC969.10

Water soluble alkali (K, Na, Ca): Soak overnight in H2O @ 90° C. Analyze by AA.

RESIDUAL OR ASH COMPOSITION
Special precautions must be taken to prepare ash fuel samples for elemental analysis so that some of the constituents will not be volatilized. Microwave digestion or wet ashing methods are preferred. ASTM D 4278, AOAC 14.7, US Bureau of Mines (Appendix B).

Ash preparation (600° C)	D 1102
Ash Elemental (Si, Al, Ti, Fe, Ca, Mg, Na, K, P)	D 3682, D2795

Optional: Ash sinter test
Heat sample in muffle furnace at 100° C intervals from 550° C to 950° C or higher and inspect for sintering.

Ash fusion temperatures	D 1857

Dirty fuels such as bark, urban wood waste, stump grindings, etc., should be screened to determine ash and alkali content of the fines: screen sample with Tyler #8 sieve, record percent of total, analyze both <8mm and >8mm.

Note: ASTM methods underlined are preferred. Refer to Appendix B for descriptions of standards and method.

Tables 4 and 5 show the fuel and ash composition of selected test fuels according to their alkali concentration. The biofuels with high annual growth, such as fast-growing woods, forest residues, prunings, annual crops and straws, all have abundant alkali in the ash. (See Tables in Appendix C.) Potassium, in particular, volatilizes and reacts readily during combustion. Wood fuels contain approximately 0.1% elemental potassium (K) compared with 1.0% or higher in straws and grasses, hulls, pits and shells. Fuel blends will of course have intermediate concentrations, as shown in Figure 12 and Table 5, but the fouling potential is not necessarily reduced due to the inclusion of other elements from the blending of fuel (Jenkins, et al.,1994). In some cases, blending can make the fouling worse.

The ash content of most clear stemwood species is less than 1%. The stemwood, or trunk, of a tree and also the larger limbs and branches contain the least alkali. The sap in the cambium layer is rich in alkali but does not deposit it in the wood itself. Clean sawdust or planer shavings from sawmills are low in alkali and high in calcium. Industrial participants report that the supply of these fuels is limited.

The furniture wood and forest residues of Table 4 and urban wood of Table 5 are typical of wood fuels received by the test power plants. Ash levels average 4% to 6% and are high in alkali, silica and calcium. Alumina is usually an indicator of dirt unless fuel processing includes cans and aluminum foil. Clean urban wood waste (UWW) consists of ground pallets, crating and construction lumber, but does pick up various contaminants. Wastes from wood processes that contain bark, dirt, or grit have higher ash, higher silica and high alkali. The urban wood fuel mixes shown in Table 5 all have high silica except for the urban wood-agricultural blend that is diluted with agricultural prunings that are low in dirt.

Ash and alkali levels are very high in the fine fuel fraction from field and urban wood residues. Fuel particles smaller than 4 mm (3/16") sift down in fuel handling and storage piles. Most of the dirt was found in the 0.85 mm (<20 mesh) fraction but requires secondary screening to remove. Experience has shown that trommel screening dirty fuels through 4 mm (3/16") dramatically decreased ash and slagging problems. Successful plants pay slightly more for fuel processors to screen fuels before delivery to the plant.

The hybrid poplar sample shown on Table 4 contains high alkali, high calcium, low ash and low silica. It also contains low sulfur and phosphorus. These are whole tree chips from 150 mm (6 in) diameter trees grown on plantations. Alkali levels are even higher when the leaves and debris, which amount to about 25% of the harvested plantation biomass, are included with the fuel. Combustion of these materials has caused slagging (Paisley, 1992).

Both trees and agricultural fuels are quite sensitive to soil chemistry and take up alkalis in particular. Table 4 illustrates high sodium and potassium in straw from wheat grown on saline soils. Sodium in high concentrations is normally toxic to non-halophytic plants, but some plants can tolerate intermediate levels where saline water is applied. The very high ash content plus moderate alkali in rice straw presents a very serious deposit and agglomeration problem as a fuel. Table 5 also shows the increase in alkali concentration when almond hulls and straw are added to wood fuels.

Table 4 Fuel and Ash Properties of Wood and Agricultural Residues

Fuel Type	Hog Wood Fuel	Furniture Wood Waste	Hybrid Poplar	Forest Residue	Switch-grass	Rice Straw	Almond Hulls	Wheat Straw Hi-alkali
Fuel								
Ash, %	1.0	3.61	2.70	3.97	8.97	18.67	6.13	9.55
Chlorine %		<0.01	.04	.04	.19	.58	.02	1.79
HHV, Btu/lb	8,998	8,658	8,178	8,670	7,766	8,123	8,119	7,228
MJ/kg	20.95	20.15	18.95	20.18	18.08	18.91	18.90	16.78
Ash composition (% weight of ash)								
SiO_2	35.18	57.62	.88	17.78	65.18	74.67	9.28	37.06
Al_2O_3	2.31	12.23	.31	3.55	4.51	1.04	2.09	2.66
TiO_2	.01	.50	.16	.50	.24	.09	.05	.17
Fe_2O_3	4.41	5.63	.57	1.58	2.03	.85	.76	.84
CaO	25.37	13.89	44.4	45.46	5.60	3.01	8.07	4.91
MgO	7.62	3.28	4.32	7.48	3.00	1.75	3.31	2.55
Na_2O	5.64	2.36	.23	2.13	.58	.96	.87	9.74
K_2O	9.26	3.77	20.08	8.52	11.60	12.30	52.90	21.70
SO_3	3.03	1.00	3.95	2.78	.44	1.24	.34	4.44
P_2O_5	5.68	.50	.15	.44	4.50	1.41	5.10	2.04
CO_2			19.52				20.12	
Undetermined	1.58	-.78	5.43	9.78	2.32	13.89	-2.89	14.32
Total, %	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Alkali								
Na_2O+K_2O, kg/GJ	.07	.10	.16	.20	.56	1.22	1.62	1.66
Lb./MMBtu	.2	.2	.4	.5	1.3	2.9	3.8	3.9

Table 5 Fuel and Ash Properties of Urban Wood Fuel Blends

Fuel Type	Urban Wood-Ag prunings, pits, shells	Urban Wood	Urban Wood-Almond	Urban Wood-Wheat Straw
Fuel				
Ash, %	2.50	5.54	6.78	8.19
Chlorine %	.05	.06	.03	.13
HHV, Btu/lb	8,379	8,361	7,928	8,083
MJ/kg	19.50	19.46	18.46	18.82
Ash Composition (% weight of ash)				
SiO_2	28.81	55.12	45.60	55.50
Al_2O_3	8.47	12.49	10.75	9.37
TiO_2	.83	.72	.54	.50
Fe_2O_3	3.28	4.51	4.06	4.77
CaO	27.99	13.53	18.96	11.04
MgO	4.49	2.93	4.22	2.55
Na_2O	3.18	3.19	3.08	2.98
K_2O	8.86	4.78	6.26	6.40
SO_3	2.00	1.92	2.06	1.80
P_2O_5	2.57	.88	1.47	1.04
CO_2	6.07			
Undetermined	3.45	-.07	3.00	4.05
Total, %	100.00	100.00	100.00	100.00
Alkali				
Na_2O+K_2O kg/GJ	.14	.21	.37	.38
Lb./MMBtu	.3	.5	.9	.9

Potassium in Biomass (TRM data)

Figure 12 Elemental Potassium in Biomass (Jenkins, 1994, from project data).

Note: potassium reported as K not K₂O.
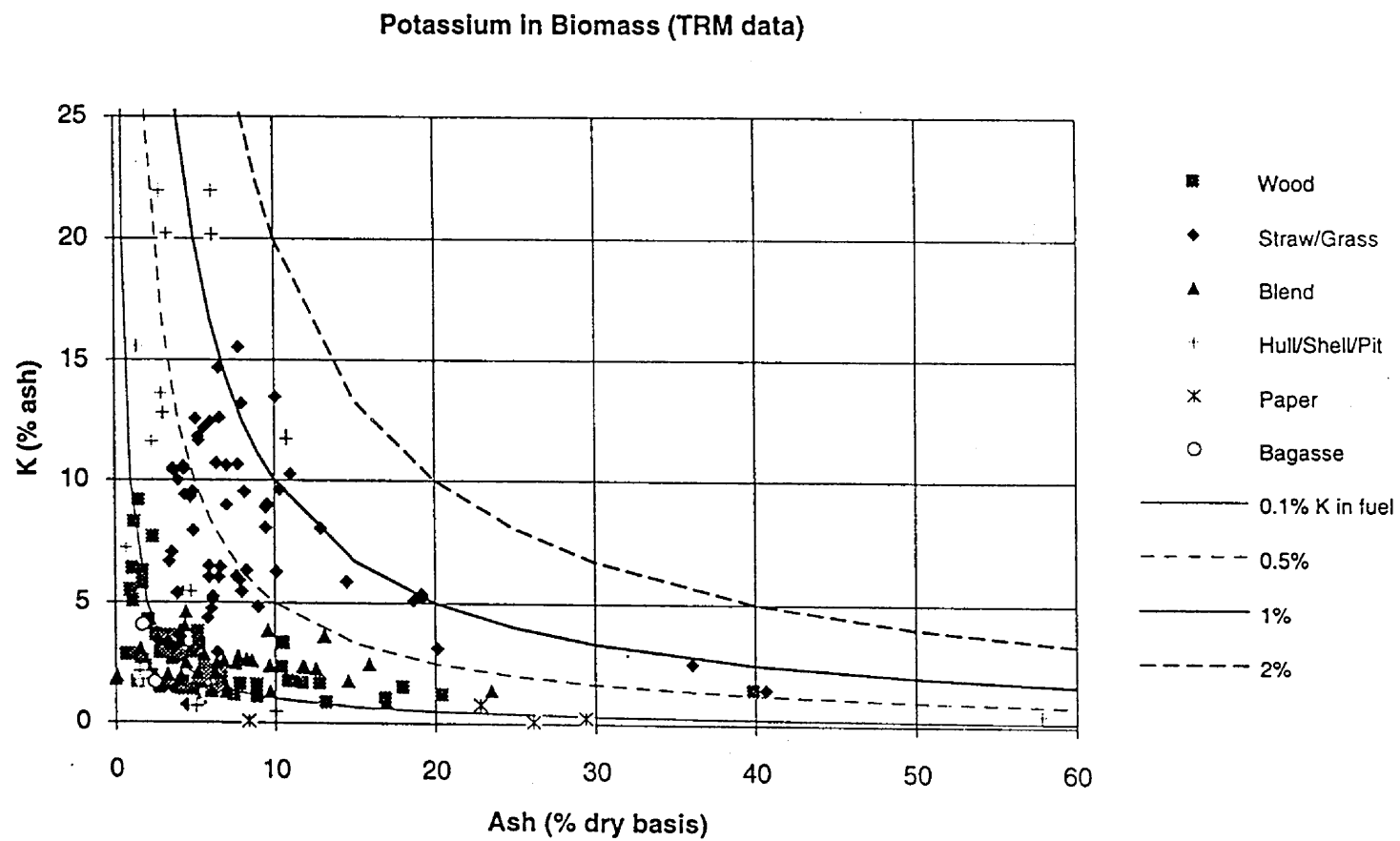
Potassium and sodium, the alkali metals, as oxides, hydroxides or in metallo-organic compounds, will form low melting compounds with silicates. Straws and grasses contain alkali and silica in proportions that promote the formation of these inorganic mixtures that melt at low temperatures. Silica alone melts at 1700° C (3100° F). Bryers shows melting temperatures for potential low-melting minerals in biomass in Appendix D.1. The phase diagram in Figure 13a shows the melting point of various mixtures of potassium oxides (K_2O), with silica (SiO_2), which makes up the bulk of the ash in biofuels. Slag in straw combustion is often associated with temperatures above 750° C (1450° F) which is near the eutectic point of 770° C (1420° F) for a mixture of 35% potassium oxide and silicon oxide as shown in the phase diagram. (Above this temperature one or both of the elements in the mixture may be liquid.) A mixture of 32% K_2O and 68% SiO_2 melts at 769° C (1420° F). This ratio is very close to the ratio of 25% to 35% alkali (K_2O+Na_2O) to silica found in many biomass ashes. An example of this melt is the glass that forms on refractory when firing straw in the spreader stokers. Bed agglomerations in fluidized bed combustors at temperatures of 760° C to 900° C (1400° F to 1650° F) are also dominated by silica which may be a result of using silica or alumina-silicates as bed media.

Figure 13 Phase Diagrams for (a) Potassium-Silica and (b) Magnesia-Silica Mixtures
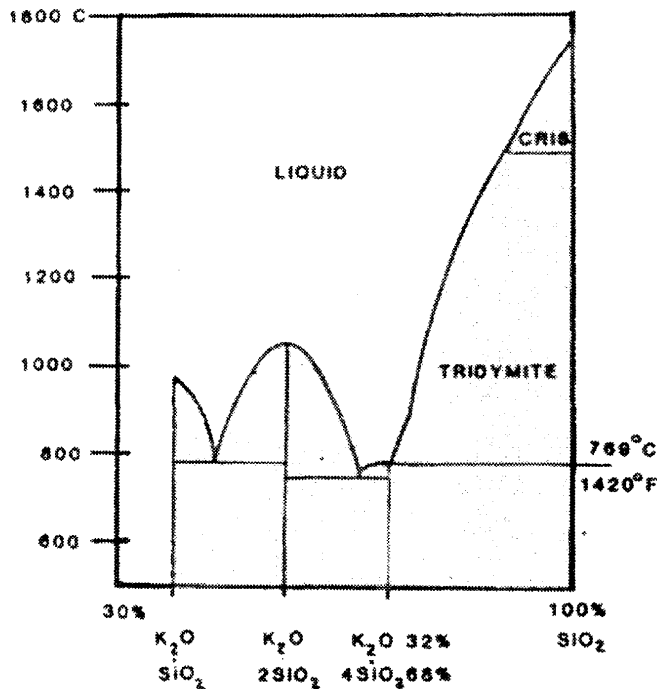
PHASE DIAGRAM FOR K2O-SiO2

AM. IRON & STEEL INST
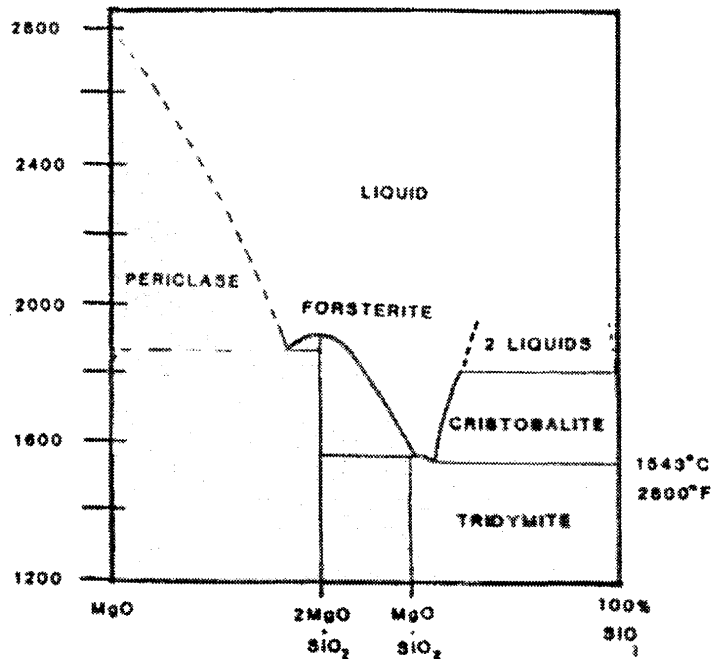
PHASE DIAGRAM FOR MgO-SIO

Chemical Fractionation

Potassium and other minerals are apparently tied up as organically bound elements, or in forms that are readily volatilized during combustion. A portion of the potassium occurs as dissolved salts in inherent moisture, cations attached to carboxylic and other functional groups, complex ions, and chemisorbed material. A substantial fraction (15%-40%) of this potassium volatilizes during combustion (Baxter, 1994).

A successive leaching test called chemical fractionation is used with coals to characterize volatile species. Two methods of chemical fractionation were used in this study to determine the fractions of the fuel that are readily volatilized during combustion. In switchgrass, for example, all methods showed that 60% to 90% of phosphorus, sulfur and potassium are potentially reactive in combustion since they are water soluble or ion exchangeable. These results distinguish biofuels from coal in which potassium may be bound in clays such as illite where it is less reactive. Sodium is the more important alkali element in coal.

Chemical fractionation data are available for almond hulls, almond shells, urban wood fuel blended with wheat straw, urban wood fuel blended with almond shells, olive pits, rice straw, switchgrass, nonrecyclable paper, and wheat straw. Duplicate samples were conducted using the same technique for switchgrass and duplicate samples using different techniques are available for switchgrass, almond shells, and wheat straw. In total, 15 samples were completed.

The procedure used for most of these samples is presented in detail in the Appendix and schematically outlined in Fig. 14. Increasingly aggressive solvents leach the same sample in a series of three sequential leachings, producing four samples (including the raw material) for characterization. Because many of the leaching steps require many hours or overnight, the overall process requires about a week of elapsed time even though it only requires an hour or two of technician time. An alternative method involving application of the leaching agents to three nominally identical samples in parallel was proposed to decrease the elapsed time required for the analysis. (See Appendix C).

The chemical fractionation technique distinguishes different types of inorganic material according to their solubility in a series of increasingly aggressive solvents. Those materials that are soluble in the two least aggressive solvents (water soluble and ion exchangeable by ammonium acetate) are the most likely to vaporize during combustion. Those soluble in hydrochloric acid are typically carbonates or sulfates. Those not soluble in any of these materials are commonly in the form of oxides, silicates, or sulfides. The mode of occurrence of the materials are important in anticipating their behavior.

Figure 14 Schematic Diagram of the Chemical Fractionation Procedure(Baxter, 1994)
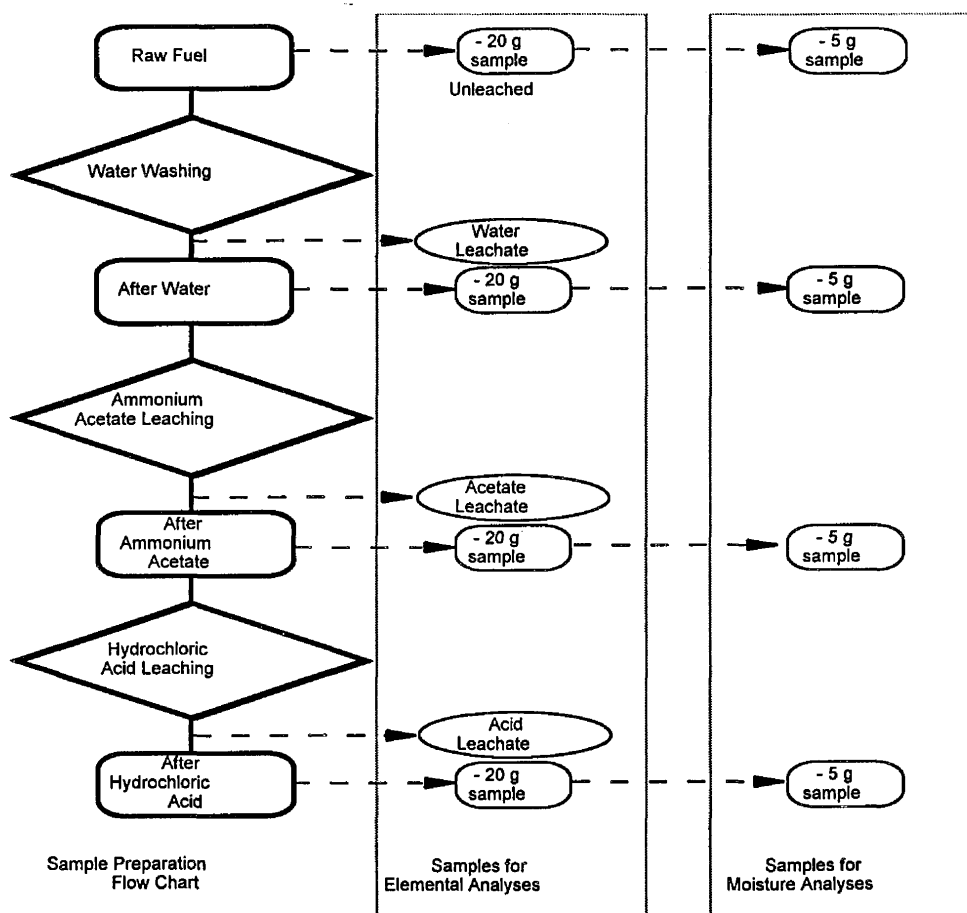
Three laboratories (US Bureau of Mines, Albany Research Center; CONSOL Inc.; and Hazen Research) were used in performing these analyses. Most of the analyses were performed by Hazen using the same procedure. These samples have no designations after their names. The fuels designated with letters B, C1, and C2 are duplicate analyses performed at different laboratories. Duplicates designated B were performed using a modified procedure. Duplicates designated C1 and C2 were each performed at the same laboratory, but a different laboratory than either the undesignated samples or those designated by B. Samples C1 and C2 were analyzed using the same procedure as the undesignated samples. Generally, there is reasonable agreement among the three laboratories. In cases of disagreement, the results from laboratory B tend to be the outlier. Nowhere is this more evident than in the titanium results for rice straw. Laboratory B suggests that titanium in rice straw is completely soluble in water, unlike titanium in any other biomass (or fossil) fuel we have tested and unlike titanium in the same fuel analyzed by a different laboratory. The titanium results for rice straw from Laboratory B may be flawed.

Figures 15 through 25 illustrate results for the 11 most prevalent inorganic components of biomass fuels (Al, Ca, Cl, Fe, K, Mg, Na, Si, Ti, S, and P). The results fall naturally into four types of elements: (1) refractory materials with little solubility (Si, Ti, and Al); (2) alkali and alkaline earth elements with varying degrees of solubility (K, Na, Ca, and Mg); (3) nonmetallic (anionic) materials typically occurring as biomass nutrients (Cl, S, and P); and (4) iron. Some of these elements are present in only trace quantities in some of the fuels.

Refractory Materials (Si, Ti, and Al)

The refractory materials Si, Al, and Ti occur in plants primarily in the form of oxides. Of the three, silicon is the dominant component. These materials are not expected to be soluble in any of the materials and should appear predominantly in the residual fraction. They also should show very little tendency to vaporize or otherwise mobilize at combustion temperatures. The data generally support this thesis. Essentially all of each of these elements is found in the residual fraction of the fuel. While these materials are reasonably refractory, silicon plays an essential biological role in many herbaceous plants. It is incorporated into the plant through biological processes, although it occurs dominantly in inorganic forms in the plant. It plays a large role in a plants' resistance to lodging (ability to remain upright in winds and rain) and overall strength and possibly a smaller role in photosynthesis.

Figure 15 Silicon Modes of Occurrence (Baxter, 1994)
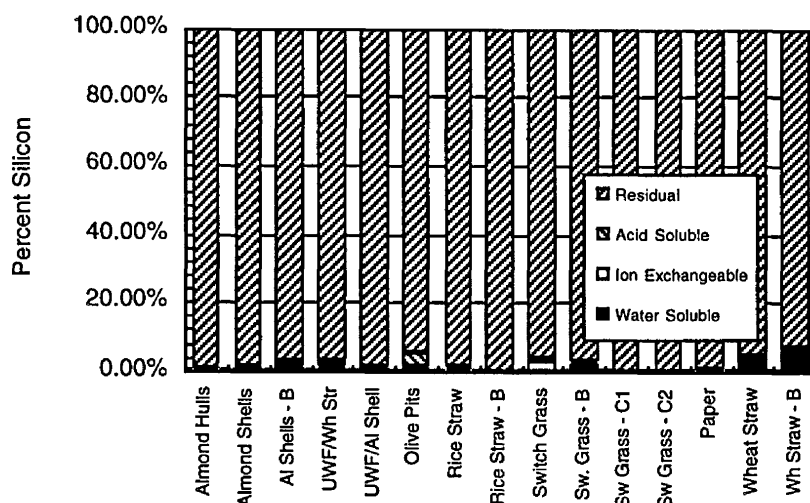
Silicon modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Silicon is a refractory material in biomass and occurs primarily as an oxide, as indicated by these data. Silicon forms a large fraction of the total inorganic material in many of these fuels.

Figure 16 Aluminum Modes of Occurrence (Baxter, 1994)
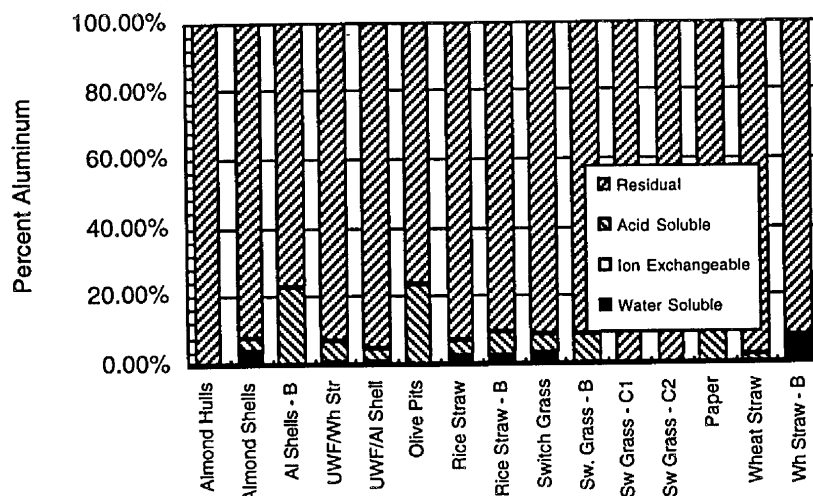
Aluminum modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Aluminum is a refractory material in biomass and occurs primarily as an oxide, as indicated by these data. Aluminum forms a small to trace fraction of the total inorganic material in all of these fuels except nonrecyclable paper.

Figure 17 Titanium Modes of Occurrence (Baxter, 1994)
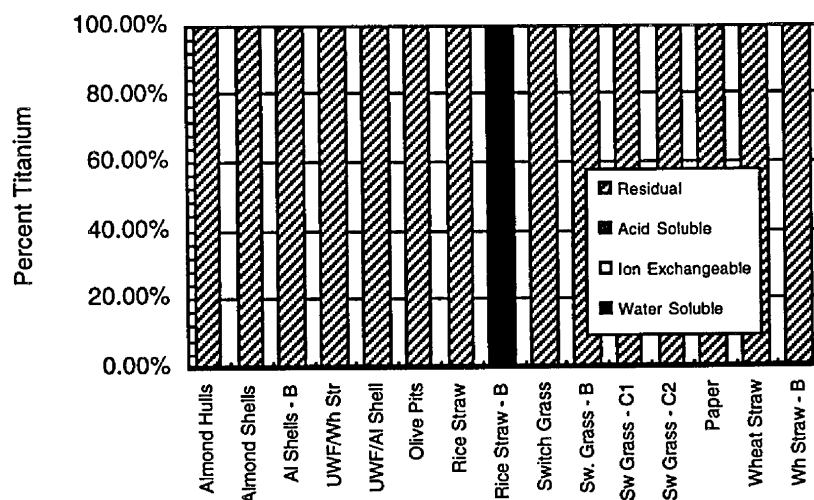
Titanium modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Titanium is a refractory material in biomass and occurs primarily as an oxide, as indicated by these data. Titanium forms a trace fraction of the total inorganic material in all of these fuels.

Alkali and Alkaline Earth Materials (K, Na, Ca, Mg)

Some of the alkali and alkaline earth materials play essential roles in plant metabolism and occur in organic structures or very mobile, inorganic forms. Potassium and calcium are the most common examples. As illustrated in Figs. 18 through 21, chemical fractionation results are consistent with the biological functions of these materials. Over 90% of the potassium of most of the clean (nonsoiled) fuels occurs as either water soluble or ion exchangeable material. Potassium is an essential nutrient in many plants and occurs primarily as a facilitator of osmotic processes, as indicated by these data. Over 90% of the potassium in clean (non-soiled) fuels occurs as either water soluble or ion exchangeable material. Sodium is a minor component of most biomass, substituting for potassium in small quantities. Calcium is a common constituent of cell walls and other organic components of cell structures, consistent with its largely ion exchangeable and acid soluble character. Calcium is also added to fuels in the form of limestone for sulfur capture and to prevent agglomeration in fluidized beds. Magnesium occurs in minor to trace quantities in most biomass material.

Both of the urban wood fuel samples were derived from commercially operating biomass boilers and contained soil contamination. Potassium and sodium are common constituents of illite, the most prevalent form of clay in soils. Nonrecyclable paper includes a large fraction of glossy print from magazines and similar publications. Similar clays are used as filler in producing these glossy prints. These are the probable sources of residual potassium in most samples.

These data indicate that much of the alkali material is found in forms that are susceptible to vaporization. In many biomass fuels, especially herbaceous fuels, potassium is the most prevalent of these materials. Its vaporization and subsequent chemical reactions are responsible for much of the fouling, sulfation, corrosion, and silicate formation found in biomass boilers. Alkaline earth materials are found in biomass in forms that are less likely to lend themselves to volatilization. Furthermore, the stable compounds they are likely to form during combustion are less volatile than for alkali materials. This explains, in part, why ligneous materials such as wood, with ash containing large fractions of calcium, pose far less fouling problems than herbaceous materials, such as straws and grass, with ash containing higher concentrations of alkali material.

Figure 18 Potassium Modes of Occurrence (Baxter, 1994)
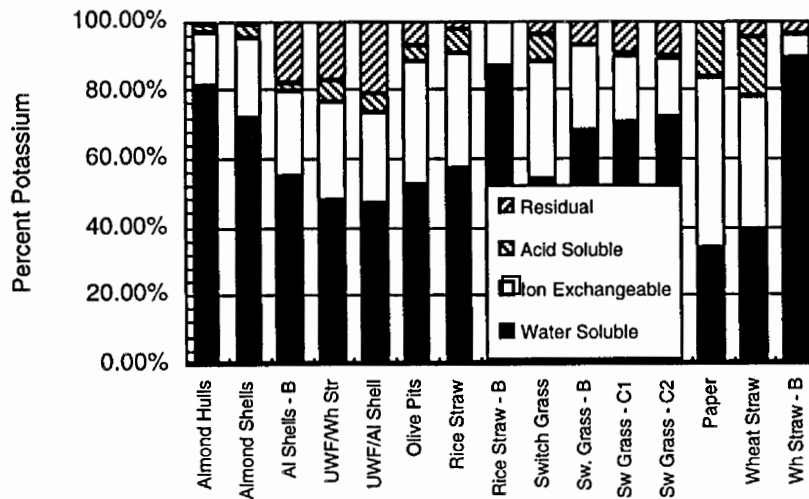
Potassium modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Potassium is an essential nutrient in many plants and occurs primarily a facilitator of osmotic processes, as indicated by these data. Over 90% of the potassium in clean (non-soiled) fuels occurs as either water soluble or ion exchangeable material.

Figure 19 Sodium Modes of Occurrence (Baxter, 1994)
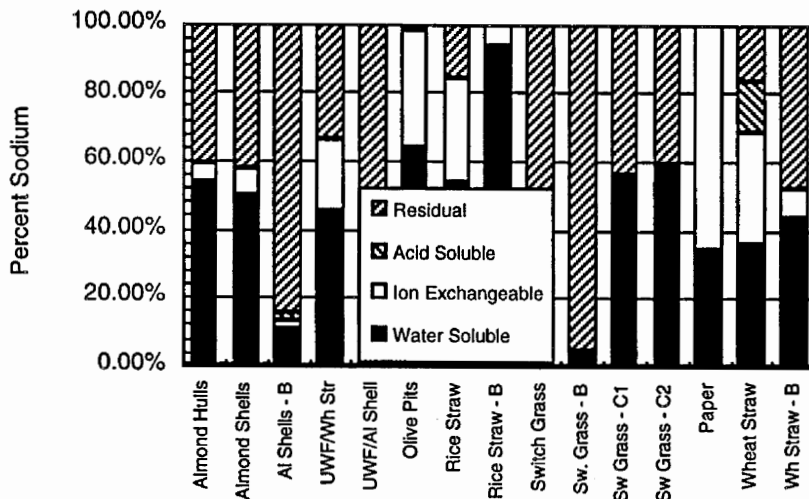
Sodium modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Sodium is minor component of most biomass, substituting for potassium in small quantities.

Figure 20 Calcium Modes of Occurrence (Baxter, 1994)
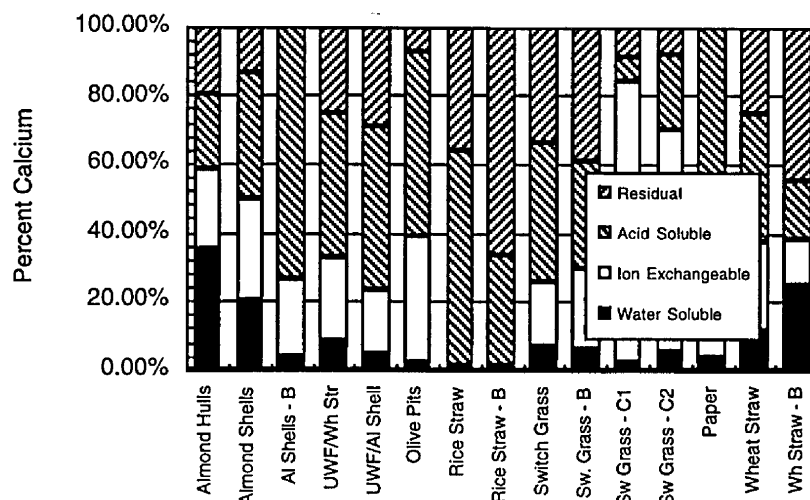
Calcium modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Calcium is a common constituent of cell walls and other organic components of cell structures, consistent with its largely ion exchangeable and acid soluble character.

Figure 21 Magnesium Modes of Occurrence (Baxter, 1994)
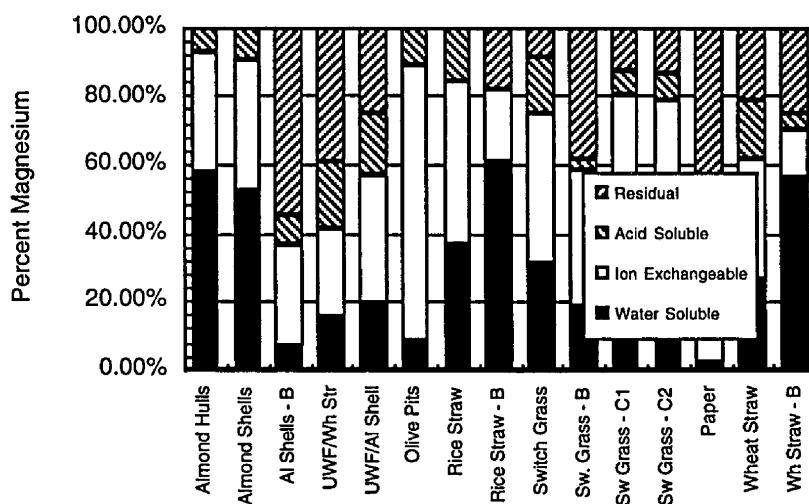
Magnesium modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Magnesium occurs in minor to trace quantities in most biomass material.

Nonmetallic Materials (Cl, S, P)

Nonmetallic (anionic) materials such as chlorine and sulfur occur as plant nutrients. The classification of nonmetallic is somewhat misleading in that none of the inorganic constituents occur as metals (i.e., in neutral oxidation states). The nonmetallic compounds tend to become anions when oxidized, by contrast to metals that dominantly form cations. However, much of the material in biomass is not ionically bound.

Chlorine plays a key role in the transformations of inorganic materials during combustion. Chlorine reacts with alkali material to form relatively volatile and stable alkali chlorides. In this process, it is commonly chlorine concentration rather than alkali concentration that limits the amount of vaporization. Condensation of the chlorides on relatively cool surfaces in the presence of sulfur often leads to the formation of sulfates. At high temperatures on many metals, this leads to a corrosive situation. Chlorine also leads to low temperature corrosion through the formation of acid gases. As indicated in the data, essentially all of the chlorine is in a vaporizable form for all fuels. The data from Laboratory B regarding chlorine are inconsistent with all of the other data and are viewed as erroneous. There are small quantities of plastic in nonrecyclable paper that contribute to forms of chlorine different from those found in traditional biomass fuels.

Stable chlorine-containing vapors generated during combustion include alkali chlorides and hydrogen chloride. The propensity of chlorine to facilitate alkali vaporization is significant. For example, chlorine is among the few materials that will react with alkali in the form of silicates. The reaction produces a gas-phase chloride. These alkali salts are both volatile and stable, and they tend to condense further downstream in a combustor than non-chlorinated alkali vapors.

Sulfur is also a major player in ash deposition. Many convection pass deposits are based on sulfate formation on tube surfaces. The general rule, that water soluble and ion exchangeable forms of material most easily vaporize, does not apply to sulfur. Sulfur, in essentially all of its forms, quantitatively oxidizes during combustion. Some of it then reacts with alkali materials to form sulfates. Alkali sulfates are unstable at typical combustion temperatures of 900° C (1650° F). These sulfates are found condensed on flyash or deposited on waterwalls parallel to the flow of gas. This primer of alkali sulfates can mix with flyash to promote agglomeration as shown in the buildup of wall deposits in the spreader stokers with travelling grates.

The behavior of phosphorus is not well characterized during combustion of these biomass fuels. It forms only a small fraction of the fuel and appears to behave as a relatively refractory material. Phosphorus is an important contributor to ash deposits from some manures and litters.

Figure 22 Chlorine Modes of Occurrence (Baxter, 1994)
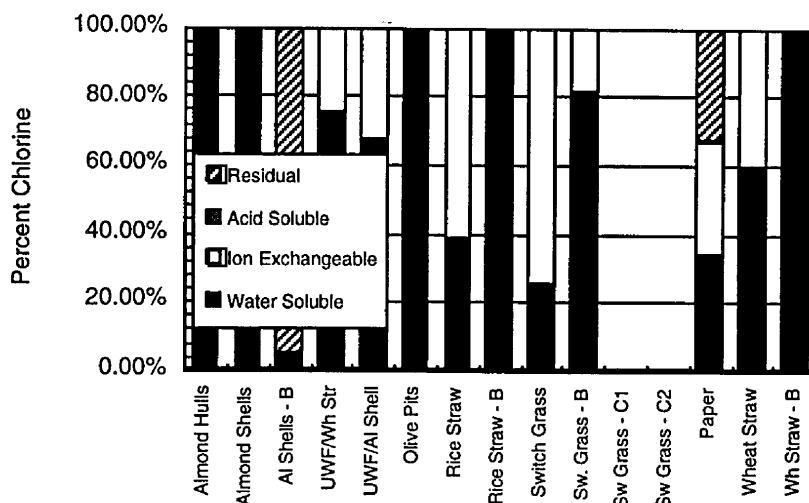
Chlorine modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Chlorine occurs in volatile forms in essentially all biomass fuels.

Figure 23 Sulfur Modes of Occurrence (Baxter, 1994)
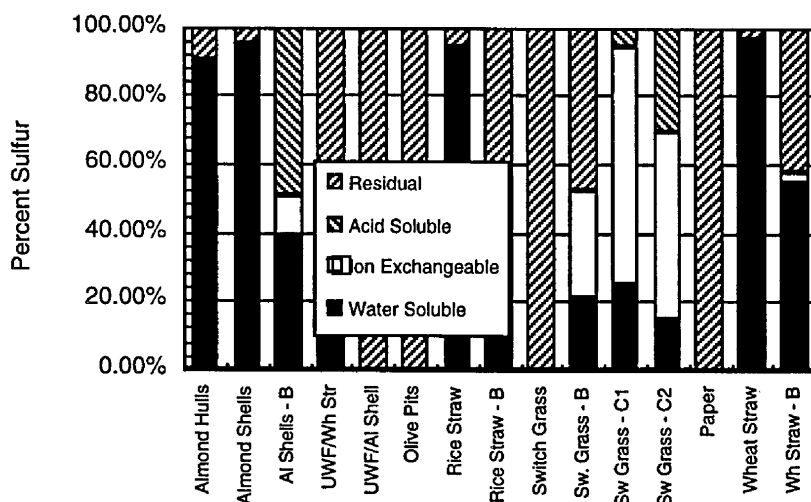
Sulfur modes of occurrence, as determined by chemical fractionation analysis, as a function of fuel type. Sulfur is a trace component of many biomass fuels but a more significant component in straws and some woods.

Figure 24 Phosphorus Modes of Occurrence (Baxter, 1994)
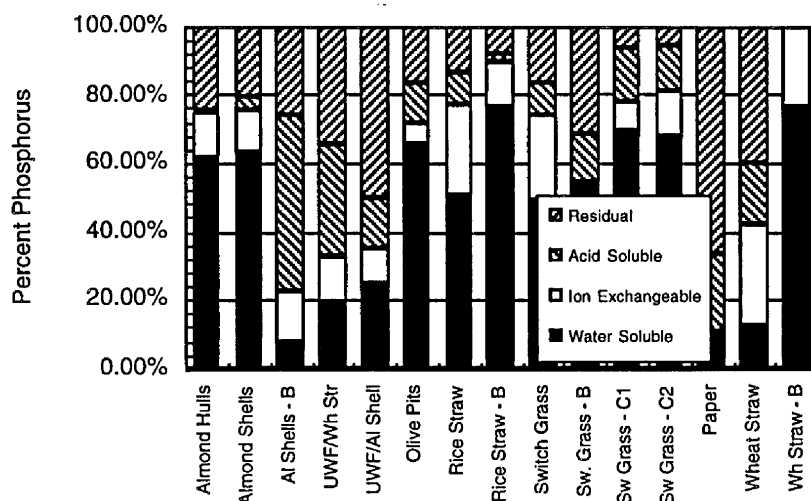
Iron (Fe)

In coal-based systems, iron plays a major role in deposit properties as an effective flux for silicate materials. In particular, the oxidation state of iron in silicates is sensitive to local conditions, with ferric iron being prevalent under oxidizing conditions and increasing amounts of ferrous iron being formed under reducing conditions. Ferrous iron incorporated in silicates leads to lower melting points than ferric iron. The typical forms of iron in coal include, in decreasing order of importance, sulfides such as pyrite, sulfates, oxides, silicates, and carbonates. Similar behavior is expected in biomass ash deposits. However, there is very little iron in the samples of biomass we have tested to date. Therefore, iron plays a minor role in ash deposits except in special circumstances. The forms of iron in biomass indicate a greater extent of ion exchangable material than is common in coal.

Figure 25 Iron Modes of Occurrence (Baxter, 1994)
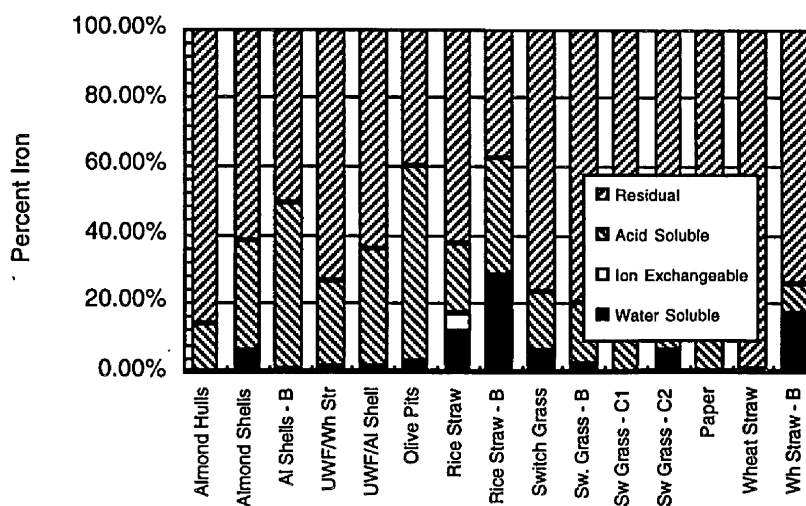
The conclusions from these results are:

(1) Chemical fractionation results show general agreement with known forms of inorganic material in biomass that is useful for anticipating the reactions such materials will undergo during combustion.

(2) Replicate samples show good, but not outstanding, agreement when performed within the same laboratory.

(3) Laboratory-to-laboratory variations can be large, although they may be attributable to lack of standard protocols at individual labs.

(4) Trends in chemical fractionation results with fuel type are rational and often reflect different processing, impurities, and other features.

The procedure followed by Laboratory B in this study was an attempt to make the chemical fractionation analysis faster, although not cheaper. The difference in the procedures was essentially to process the fuel through the various stages in parallel rather than sequentially. In principle, the parallel approach should be fine. In practice, it appears to have significantly compromised the results. This may be because of inherent sample-to-sample variations in biomass – a concern noted at the outset. However, the first step of both processes (water washing) is essentially identical. Many of the differences in results from Laboratory B appeared in this first step. This suggests that the problem lies more in the laboratory analyses than in the procedure.

ASTM Ash Fusion Tests and Other Methods of Ash Analysis

Fuels and deposits in these tests demonstrated that standard ash fusion temperature analyses are not useful for predicting deposit behavior in biomass for several reasons. First of all, the American Society of Testing and Materials (ASTM) ash fusion test does not simulate boiler conditions, where alkali that volatilizes during combustion concentrates as it condenses on silicate refractory or flyash. Secondly, substantial alkalis are lost during the ashing process in preparing pyrometric cones for ash fusion temperatures, thereby artificially raising the measured fusion temperature. High temperature ashing vaporizes much of the alkali as does prolonged calcining. For example, coal samples are ashed at 750° C and calcined at 1000° C. Measurements of potassium in biofuels were found to be 15% to 25% lower when they were ashed at these high temperatures. Also, in the boiler, vapor phase K and other compounds are continuously generated and are available for reaction with deposited materials. The ASTM test does not simulate this feature. Samples should be ashed at 600° C with no calcining, following ASTM D1102 or E830 (TAPPI, 1992).

Low temperature ashing using oxygen plasma was tested as an alternative to the ash fusion tests but produced compounds that are not characteristic of biomass heating or combustion. Differential thermal analysis (DTA) and themogravimetric analysis (TGA) of fuel ashes did not correlated well with deposit composition. Further analysis of biomass deposits and flyash are needed (Bryers, 1994). Analysis of water soluble alkali in the fuel, or wet digestion followed by elemental analysis, resulted in more reliable alkali data than thermal ashing methods. A method that was developed by the Bureau of Mines for the project accounted better quantitatively for all of the elements in the fuel sample compared with standard thermal methods (Oden, 1993). See Appendix B.

4. DEPOSITS

Power plants in the project experienced the same fireside deposits and convection pass fouling that have reduced plant availability and efficiencies in the industry. Deposits were sampled from operating plants at the end of a four to six month firing period. Laboratory samples were collected on air cooled probes in the Sandia Multi-Fuel Combustor. All samples were analyzed following a common format, including routine analysis for selected chemicals, proximate and elemental ash composition. Selected samples were analyzed by X-ray diffraction and scanning electron microscopy (SEM). See Appendix B for methods.

Power plant deposits occurred on the grate, in the bed or on refractory as hard fused glassy deposits, agglomeration of grate ash or bed media, and as accumulations of flyash in hot gas ducts. Fouling of the boiler convection passes included buildup on screen tubes or superheater tubes, bridging between tubes, and hard deposits on tubes. Sootblowing sometimes removed buildup, but coverage was often not adequate. Deposits on convection surfaces developed quickly when furnace exit temperatures exceeded 750° C (1450° F). Corrosion was found under many deposits. Deposits collected from similar temperature zones in different boilers had similar compositions. Grate and wall deposits were similar in composition to the fuel ash. Potassium and calcium silicates and sulfates deposited on screen tubes and upstream superheaters. Chlorides and carbonates appeared in the cooler convection passes. Detailed descriptions of deposit mechanisms observed in the project are discussed by Bryers (1994) and Jenkins, et al. (1994). Tables 7-9 show analyses of deposits found in fluidized bed and traveling grate boilers from the tests.

Elements from the fuel deposit in several different forms in boilers. High silica slags frequently form in the high temperature furnace regions as alkali and alkaline earth metals react to form molten composites and glasses. Slag masses can form and accumulate on grates or running slags may form on walls, especially refractory walls with high surface temperatures, but also on waterwalls. Wall slags are commonly seen in the vicinity of the fuel feed ports. Slags can form as rock-like, ribbon-like, hair-like, or other structural forms. Agglomerates also occur, composed of sand and ash particles bound by fused, glassy materials arising from reactions between the fuel elements or other compounds in the furnace. Agglomeration is a common problem in fluidized bed combustors, where reactions in the bed can lead to the formation of large aggregated composites of bed media and ash, with eventual defluidization of the bed and plant shutdown. Fireside fouling deposits occur on all heat transfer surfaces, but especially on cross-flow tubes situated in the convection passes of boilers. Fouling of furnace waterwalls in fluidized beds has not typically been of concern because of the active abrasion by bed media particles. Fouling of waterwalls in the convection passes occurs routinely, however, although not generally with the same severity as cross-flow tube surfaces. Particle separation devices, such as cyclones, located at the furnace exit in circulating fluidized beds are also subject to severe fouling.

Figure 26 Deposits block gas flow in tertiary superheater causes erosion and reduces heat transfer. Wood-Ag Blend. FBC-1.

Gas Flow
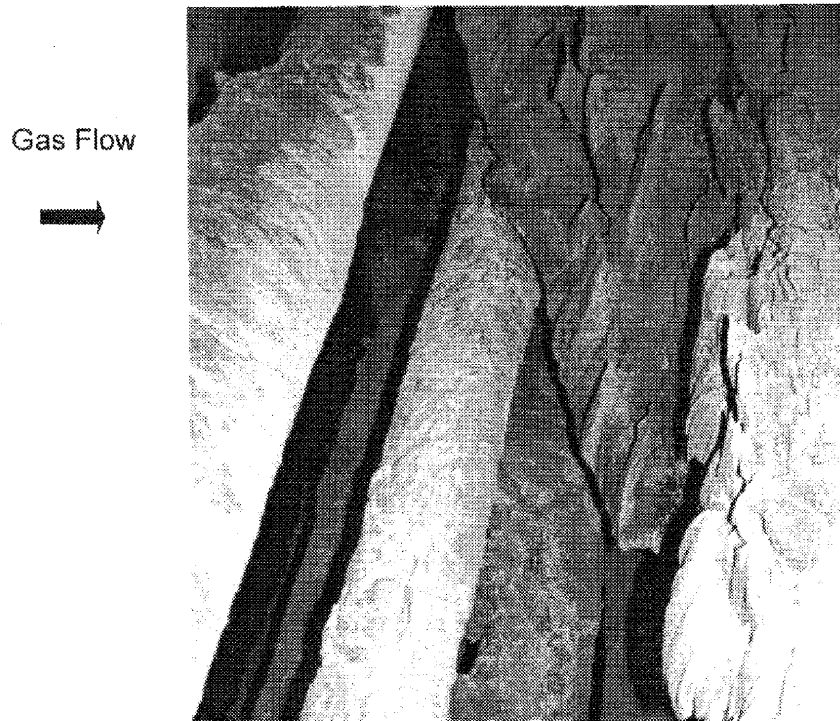
Figure 27 Deposits fill openings between convection tubes, reducing heat transfer in secondary superheater. Wood-Pit Blend. CFB-3.

Gas Flow
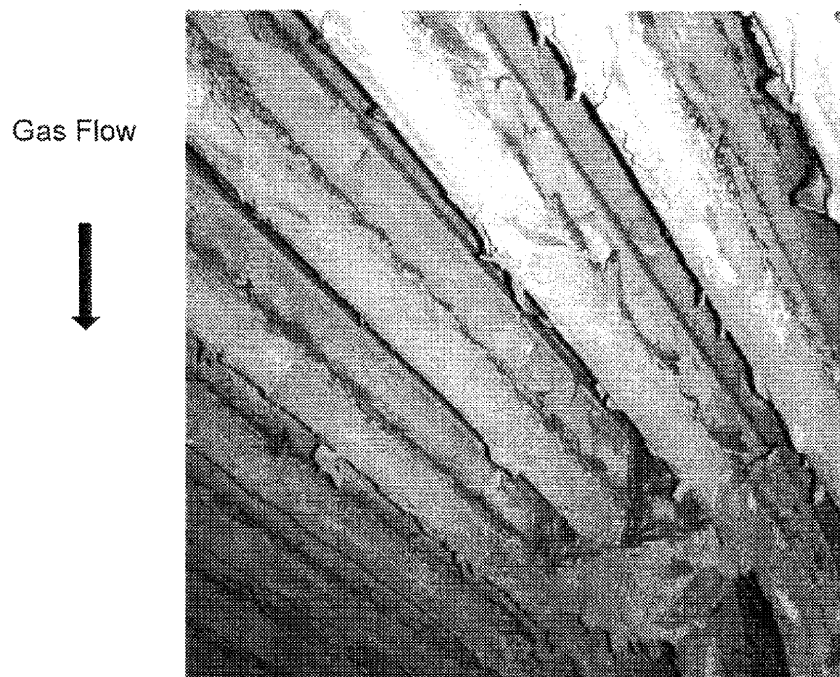
The apparent mechanisms of fouling deposit formation on boiler surfaces include condensation of inorganic vapors, inertial impaction and sticking of particles, thermophoresis and possibly electrophoresis, and chemical reaction (Raask, 1985, Baxter, 1993). The order in which these occur, and the relative rates, are important to the morphology and mechanical properties of the deposits. There are three principal undesirable effects of deposits: 1) deposits retard the heat transfer and lead to an eventual decline in boiler efficiency and capacity if they cannot be removed according to the design assumptions for the boiler, 2) deposits can grow to the extent that flow through the boiler is restricted, often bridging across tubes and tube bundles, and causing mechanical damage, and 3) deposits are associated with corrosion. Deposits which are less tenacious and easily removed (e.g., by soot blowing), represent less of a problem to facility operators than those which are hard to remove, and require shutting down the boiler for cleaning.

Alkali and alkaline earth metals in the fuel ash are important to the formation of fireside deposits. For biomass, potassium is the major alkali element of concern. By contrast, sodium is the most troublesome alkali component for most coal-fired systems. Both potassium and calcium are important in the formation of sulfate deposits on boiler surfaces. Straws, other grasses and herbaceous species, younger tissues of woody species, nut hulls and shells, and other annual biomass contain about 1% potassium dry weight (Figure 12). Potassium is a macronutrient for plants. Along with potassium, straw invariably contains a substantial amount of chlorine, usually at levels greater than 0.2% and up to 3% dry weight (Jenkins, 1989). Straw also contains substantial amounts of silica, usually in macronutrient concentrations. The role of minerals in plant nutrition has been described by Marschner (1986). Rice straw, for example, contains about 10% of dry weight as silica. By itself, silica does not present much of a problem for biomass boilers. Rice hull, which may contain 20% by weight silica, does not easily slag and foul in boilers when fired alone because the ash is relatively pure in silica (> 95% SiO_2 in ash, typically) and the melting point is high (> 1650° C), although there exist other problems related to crystalline transformations and the atmospheric emission of cristobalite, a known respiratory hazard, if combustion conditions are not properly controlled. Silica in combination with alkali and alkaline earth metals, however, especially with the readily volatilized forms of potassium present in biomass, can lead to the formation of low melting point compounds which readily slag and foul at normal biomass boiler furnace temperatures (800° C - 900° C). Chlorine can be an important facilitator in fouling, leading to the condensation of alkali chlorides on heat transfer surfaces in the boiler, and promoting the development of alkali sulfates. Chlorine may be an important element in the vaporization of alkali species, leading to the formation of more severe deposits. Sugar cane bagasse, which has long been used successfully as boiler fuel, and which is derived from another high potassium, high silica herbaceous crop, does not exhibit the same fouling tendencies as straw and sugar cane trash (tops and leaves) because both potassium and chlorine are substantially leached from the fuel in the process of extracting sugar.

Unlike straw, wood contains very little silicon, and the mature stem wood that makes up the majority of wood fuel, including urban wood fuel, also contains substantially lower amounts of potassium, usually only about 0.1% dry weight (Figure 12). Potassium is a highly mobile element in plants, and moves to younger, actively developing tissues, leaving the mature stem wood depleted in potassium. Facilities

burning the leaf and branch fractions of wood, or coppice materials from short rotation woody cultures (SRWC), will also encounter higher levels of potassium (as well as nitrogen and sulfur) in the fuel. This is already apparent in the agricultural wood fuels (e.g. annual prunings) currently burned in boilers. Although wood fuels are inherently low in silica, adventitious material such as clays and other soil components brought in with the fuel include silica and can lead to fouling, although usually at reduced rates compared to straw. Urban wood fuels can include substantial amounts of adventitious materials from manufactured products. The chemistry of inorganic transformations in boilers is quite complex, involving multiple physicochemical pathways among alkali, alkaline earth, and other inorganic and organic species in the fuel. The principal components of interest include silicon, potassium, chlorine, sulfur, iron, phosphorus, magnesium, calcium, titanium, carbon, hydrogen, and oxygen. Sodium and aluminum, which are not normally found in inherently high concentrations, may be introduced as soil or through prior processing operations, as with sodium in olive pits, and may also influence the fouling behavior. For most biomass fuels, the elements silicon, potassium, calcium, chlorine, sulfur, and to some extent, phosphorus, appear to be the principal elements involved in the fouling of boiler surfaces.

Deposit formation also depends on the boiler design and operation. Differences in slagging and fouling behavior have been observed for the various types of grate, fluidized bed, and suspension boiler designs. Superheater fouling depends to a large extent on the furnace exit gas temperature, a feature recognized by industry in the control of fouling deposits. Many existing biomass boilers were designed with high furnace exit gas temperatures (900° C or higher). Coupled with cross-flow superheaters typically employed, severe fouling is frequently observed. Reducing the temperature to control deposits can lead to derating the boiler with undesirable economic consequences. Other designs utilizing extended parallel flow heat exchangers or tube walls have been used with some success to reduce the fouling severity, as noted below.

This section describes certain characteristics of deposits recovered from the commercially operating biomass boilers, as well as those collected during controlled laboratory combustion experiments using similar fuels and others not burned commercially, including straw. The analysis of these deposits was undertaken as part of the Alkali Deposit Investigation and reported by Jenkins, et al. (1994). The laboratory combustion experiments were conducted at Sandia National Laboratory, Livermore, California, also under sponsorship from NREL. Chemical compositions of deposits from the laboratory experiments are reported, and compared with the composition of deposits from commercial boilers. The laboratory results are observed to be consistent with full-scale results, as well as with the perceived mechanisms of deposit formation mentioned above. The results suggest some limited short term strategies for mitigating deposition on convective surfaces in existing units through furnace temperature control.

Procedures

Full-scale experiments:

Deposit samples were collected from 7 different biomass power stations. Three of the boilers employed grate-type furnaces, one was a bubbling fluidized bed, and three were circulating fluidized beds. The plants ranged in capacity from 5 to 25 MWe. The main features of the boiler designs are illustrated in Figures 1 and 4 (pp. 6, 8).

Two of the grate units (later identified as Grate-2 and Grate-3) were located in Denmark and fired straw, principally wheat straw. All other boilers were located in California. Fuel supplies for all of the units vary with season and availability. During these tests, Grate-1 fired a mixture of wood (80%) blended with wheat straw (20%). The bubbling fluidized bed unit (FBC-1) fired a blend of 60% urban wood fuel, 37% agricultural wood, and 3% almond shell. One of the circulating fluidized beds (CFB-1) fired a blend of wood (from urban and agricultural sources) with 6% almond shell, another (CFB-3) fired a blend of sawdust with 20% pits, shells, and hulls in varying concentrations, and CFB-2 fired a variable blend based on wood with additions of pits and shells (Figure 4). For CFB-2, composite fuel samples were collected during each week and analyzed only for chlorine, sulfur, and water soluble calcium, potassium, and sodium.

The essential configurations of the boilers are similar, with waterwall furnaces followed by cross-flow superheaters, economizers, and air-heaters in the convection passes. The circulating fluidized beds are distinctive in the inclusion of particle separation devices at the furnace exit for the purposes of recirculating bed material and partially burned fuel back to the bed. CFB- 1 and CFB-2 are identical designs of identical capacity, and utilize twin cyclones for particle separation. CFB-3 utilized a series of cross-flow impaction surfaces (U-tubes) to disengage particles from the furnace exit flow. A more important distinction lies in the folded furnace design of the two Danish units, by which the furnace section is extended and the gas temperatures ahead of the cross-flow superheaters are reduced substantially compared to the California units.

Deposits were collected following routine operation of the boilers for periods up to 4 months. Fuel and ash samples were collected throughout the experiments. For the purposes of conducting the investigation, an attempt was made by the operators of CFB-1 and FBC- 1 to maintain a reasonably constant fuel composition. The fuel composition for Grate-1 was strictly controlled. Fuel mix was adjusted routinely for the other facilities. As a result of firing only straw, the fuel compositions for Grate-2 and Grate-3 were essentially fixed. The greatest variability in fuel mix occurred with CFB-2. CFB-3 was operated on an intermittent basis, running at peak capacity under utility dispatch, and curtailed off-peak. The other facilities were all operated at or near their peak capacities.

Results of deposit composition assays are described here for the purposes of comparison with the results from the laboratory experiments. As shown later, laboratory results, although from tests of much shorter duration and with only general similarity in combustion and flow conditions to the full-scale boilers, appear to be consistent when interpreted in light of the major mechanisms proposed for the formation of fouling deposits.

Laboratory experiments:

Small deposit samples were obtained by burning various biomass fuels in the multi-fuel combustor (MFC) at Sandia National Laboratory, Livermore, California. The multi-fuel combustor was originally designed to simulate pulverized coal combustion and ash deposition in utility systems. The combustor, depicted in Figure 28, is a 4.2 m high vertical tube furnace 15 cm in inside diameter. The upper six of seven furnace modules are independently electrically heated. The furnace duct is open at the bottom, discharges across a 0.7 m high open space into the inlet of a large duct, which also draws laboratory air for dilution and cooling prior to exhaust. In the test section, various probes can be inserted into the furnace or across the furnace exit flow. A natural gas burner situated at the top of the furnace supplied a preheated oxidant stream to the furnace to aid in simulating full-scale furnace conditions. Milled biomass fuel passing a 10 mesh or finer sieve was injected pneumatically via a water-cooled lance inserted through the side of the furnace just below the top. The fuel was fired downward from a position about 4 m above the test section, producing a particle residence time of 1 to 2 s. For all tests reported here, the furnace wall temperature was set at 900° C to simulate a typical biomass combustor furnace exit gas temperature ahead of the superheaters.

The fuels used for the MFC experiments included almond hull, almond shell, olive pits, rice straw, switchgrass, wheat straw, and a blend of urban and agricultural wood fuel with almond shell. The latter was the same fuel burned by CFB- 1. The compositions of these fuels are listed in Table 6 following. The fuels selected provided a wide range of inorganic element concentrations.

Deposits were collected on a horizontal 16 mm o.d. steel tube situated across the furnace exit flow. In most experiments, this deposit probe was continuously rotated for the purpose of obtaining emission spectra from the deposit for analysis by FTIR. This nondestructive technique provides time resolved in situ information on deposit composition and other properties, but is developmental for biomass and the results are not discussed here. Alongside the rotating probe, a stationary horizontal tubular probe of the same diameter was inserted to collect additional deposit and to better simulate the stationary superheater surfaces in commercial boilers. Deposition on a vertical furnace or convective pass waterwall surface was simulated by inserting a simulated waterwall in the test section extending upwards into the furnace. The waterwall probe consisted of a serpentine steel tube with membranes between each bend. All probes were air cooled and thermocouple instrumented, with surface temperatures maintained in the range of 400° C to 500° C, to simulate the wall temperatures of heat exchangers in full-scale units.

Natural gas
Combustion air
Preheat Burner
Flow straightener
Fuel lance
Pneumatic fuel transport

15 cm

Heater element
Insulation
Liner

Instrument port

Heater Module

0.6 m

Surface thermocouple
Open test section

Rotating deposit probe
Stepper motor
Instrument table

To exhaust blower
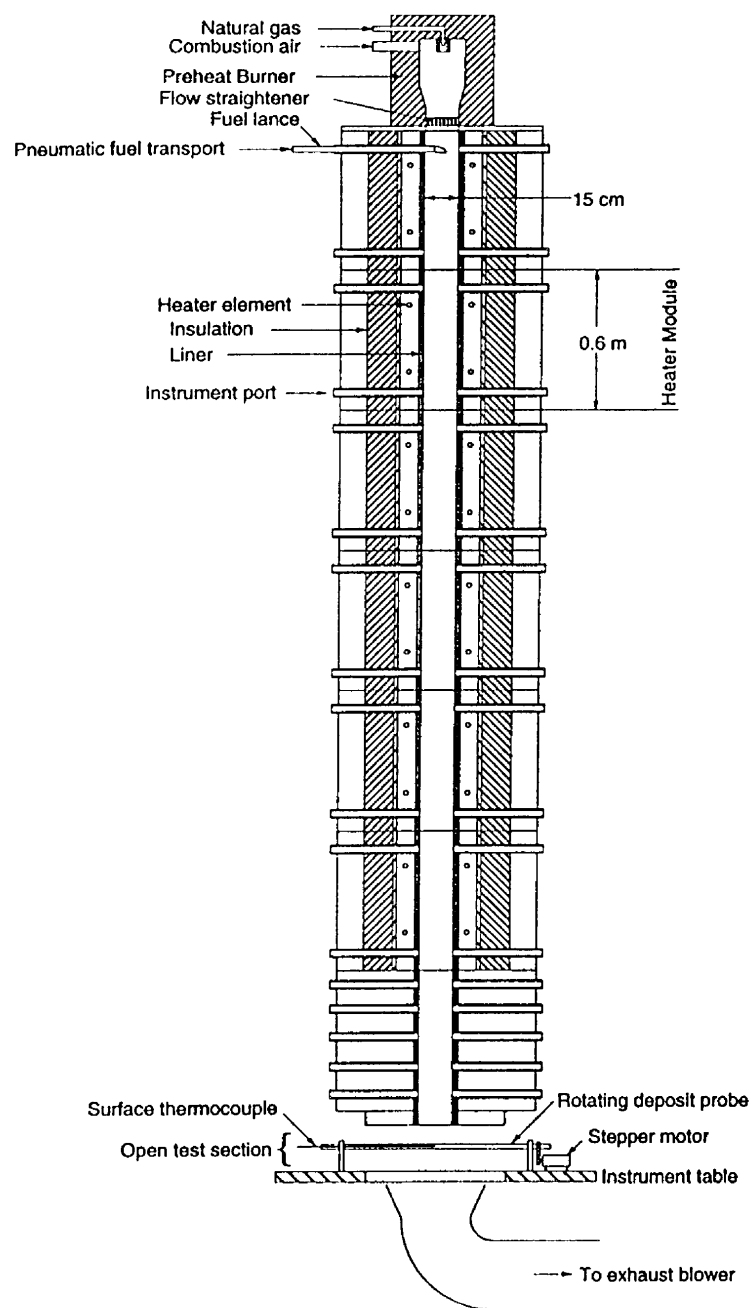
Table 6 Composition of Fuels Used in MFC Tests

Fuel	Almond Hull	Almond Shell	Olive Pits	Rice Straw	Switch Grass	Wheat Straw	Wood/Shell Blend
Chlorine % dry fuel	.06	0.03	0.08	0.51	0.10	0.19	0.3
Ash, %	6.16	3.07	1.91	20.34	4.57	8.09	7.25
Ash Composition (% ash as oxide)							
SiO_2	6.03	9.82	31.47	80.15	69.21	67.54	55.69
Al_2O_3	1.28	2.44	6.45	1.46	3.84	2.14	10.75
TiO_2	0.07	0.10	0.31	0.06	0.14	0.10	0.52
Fe_2O_3	.83	2.46	6.97	0.85	1.52	1.22	4.72
CaO	8.66	11.95	13.66	2.03	8.17	3.08	14.04
MgO	5.01	4.35	4.48	2.11	3.48	2.88	3.01
Na_2O	0.99	1.61	27.43	0.91	.082	2.05	2.17
K_2O	53.60	44.72	1.77	8.51	7.26	14.38	4.39
SO_3	1.46	6.52	1.98	1.22	1.49	5.02	1.54
P_2O_5	7.33	1.41	3.34	1.68	3.63	1.41	1.11
Undetermined	14.74	14.63	2.12	1.02	0.14	0.18	2.06
Total, %	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Und = undetermined

Figure 29 Wheat Straw Deposit Accumulation on MFC Simulated (air cooled) Boiler Tube
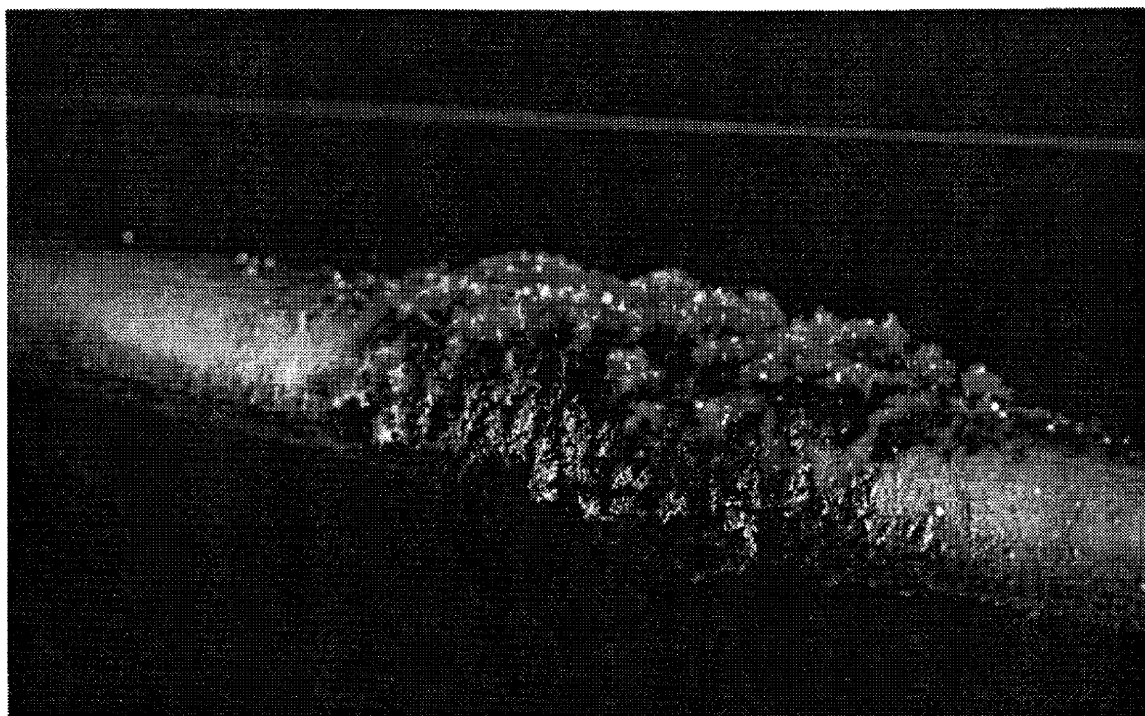
Flyash samples were collected from the flow just ahead and to the side of the deposit probes through a water cooled, helium quenched nozzle. Flyash was collected on 127 mm diameter, 1 micron pore size polycarbonate filters. Flyash samples were collected without a size selective inlet. Often large, partially oxidized fuel particles were collected loose in the filter holder, and were generally analyzed separately. Such particles were also frequently collected on the horizontal surfaces of the waterwall probe, and were analyzed separately.

Straw and grass fuels produced rather heavy deposits on the furnace wall downstream from the fuel injection point. In the case of rice straw, these deposits grew inwards to a point where aerodynamic drag or furnace vibration caused them to fall from the wall. Deposit attrition from wall deposits falling and impacting the probes caused a second rice straw test to be aborted. Wall deposits were collected and analyzed separately.

Each test lasted three to six hours, and consumed 3 to 10 kg of fuel. Deposit samples were collected from the probes at the end of each experiment and submitted for chemical analysis. In most cases, the deposit weight was not more than a few hundred mg, and was inadequate for chlorine analysis. For the straw fuels known to contain higher amounts of chlorine, scanning electron microscopy (SEM) with energy dispersive X-ray analysis was used to analyze for major elements in deposits.

Results

Full-scale experiments:

Elemental compositions for selected deposits taken from the commercial boilers appear in Tables 7 through 9 (pp 45-53) by boiler type and in Appendix C. Included in the tables are average fuel ash compositions during each experiment that produced the deposits. Concentrations are reported for elements, except Cl, in the conventional oxide form, although the elements do not necessarily exist as oxides either in the fuel or the deposits. By reporting the concentrations as oxides, the total recovery can be tentatively assessed to identify either the quality of the analysis or the possible undetermined presence of other species. The undetermined (Und) fraction listed for each analysis is simply the difference between 100% and the sum of all species. For two of the CFB units (CFB-1 and CFB-3), the composition of the bed media is also reported. The other fluidized beds used similar material to CFB-1. FBC-1 and CFB-1 added limestone to the bed at rates between 100 and 200 kg h^{-1}. CFB-2 added spent lime from the water treatment system and occasionally limestone for the first two months of the test, and none thereafter. CFB-3 did not add limestone. Cl and carbonate (as CO_2) concentrations were not analyzed for Grate-1, while carbonate was analyzed for only three of the CFB-1 samples and none of the CFB-3 samples.

Grates

For Grate-1 (Table 7), compositions are shown for three typical deposit types: the upstream superheater surfaces, a white reflective deposit collected from the upper

furnace wall in a corner opposite the entrance to the convection pass, and a slag removed from the grate of the furnace. These deposits were formed during a five day period. During the first three days, the boiler was operated at partial load due to materials handling problems related to feeding the wheat straw. After attaining full load, the boiler operated only two more days before it was shut down due to severe slagging on the grate and failure of the ash handling equipment. The nature of the deposits has been described in some detail by Baxter, et al. (1993) and Miles, et al. (1994). The deposit compositions are summarized here for comparison. The grate slag for the most part bears a close resemblance to the fuel ash composition, whereas the furnace wall and the superheater deposits are markedly dissimilar. The low sulfate concentration of the grate slag suggests that nearly all sulfur was volatilized.

Relative to the fuel, the superheater deposits are substantially enriched in potassium and sulfur, and depleted in silicon. The relative concentration ratio or elemental abundance obtained as the ratio, Cid/Cif, of the concentration of oxide or element in the deposit, Cid to the concentration of the same oxide or element in the fuel ash, Cif is depicted in Figure 30 (SiO_2 through P_2O_5) and Figure 31 (SO_3, Cl not measured) for the superheater deposit. In computing the relative abundance, the concentrations were normalized by the total determined fraction to remove the influence from differences in the undetermined fraction. This has little effect due to the good recoveries for the analyses. The deposit from the upper furnace wall is composed almost entirely of alkali sulfates. Due to the design of the boiler, this corner of the furnace was located in a recirculation zone with poor convective transport and subject primarily to condensation of inorganic vapors or diffusion of small particles. The deposits show little influence from particle impaction and sticking. White deposits of similar appearance were observed to form initially on the screen and superheater tubes during partial load operation. The final superheater deposit composition shows an apparent influence from increased deposition of ash particles, the result of impaction, as well as reaction between sulfur and alkali species and calcium in the formation of sulfates. Thermophoretic deposition may also have been important in the initial deposit development on the superheater and screen surfaces.

The superheater deposits from the wheat straw-fired boilers (Grate-2 and Grate-3 in Table 7) are enriched in potassium, chlorine, and sulfur relative to the fuel (the same fuel composition is used for both facilities), indicating the presence of alkali chlorides and sulfates. The relative abundance of elements in the upstream superheater deposits is shown for each unit in Figures 30 and 31. The rather large enrichment in iron for Grate-3 may be due to the inclusion of tube metal in the deposit when sampled. A deposit collected from the upper furnace wall of Grate-3 just ahead of the first fold in the furnace section also shows enrichment in potassium, chlorine, and sulfur. Another deposit collected from the front nosewall of the furnace just above the stokers more closely resembles the fuel ash, although it is enriched in calcium. The grate slag taken from Grate-2, like that from Grate-1, bears a close resemblance to the fuel ash, but also is enriched in calcium. The higher chlorine concentration in the wheat straw fuel compared to the wheat straw/wood fuel blend of Grate-1 yields greater quantities of potassium chloride in the deposits judging by the sulfate ratios in the deposits among the three facilities. The mass ratios of potassium to chlorine and to sulfate in Grate-2 and Grate-3 superheater deposits are consistent with the presence of potassium as chloride and sulfate.

Table 7 Composition of Fuels and Deposits, Grate Type Boilers

	GRATE -1				GRATE -2			GRATE -3		
	Fuel	Super-heater	Upper Wall	Grate Slag	Fuel	Super-heater	Grate Slag	Super-heater	Upper Wall	Front Nosewall
Ash Composition (% ash as oxide)										
SiO_2	57.58	33.77	5.41	60.75	63.45	18.62	62.26	10.64	7.54	49.51
Al_2O_3	10.16	9.47	1.63	10.72	1.95	1.12	1.94	0.99	1.55	2.16
TiO_2	0.48	0.50	0.07	0.56	0.02	0.02	0.07	0.02	0.02	0.05
Fe_2O_3	3.98	3.57	2.74	3.79	0.66	0.32	0.48	8.73	0.52	0.66
CaO	11.29	14.68	4.97	11.25	4.20	14.41	10.59	4.80	3.79	15.09
MgO	2.96	3.79	1.26	3.23	0.46	2.45	2.15	0.80	0.08	2.71
Na_2O	3.04	4.09	9.05	2.32	0.83	0.47	0.47	0.97	1.12	1.58
K_2O	6.89	11.80	27.90	6.01	13.10	33.40	17.70	43.50	51.20	18.70
SO_3	2.26	16.30	41.90	0.13	1.95	8.67	0.04	3.90	5.99	0.20
P_2O_5	1.07	1.12	0.76	1.28	4.96	3.46	3.74	1.29	1.06	3.94
Chlorine *	1.91	0.21	0.01	0.01	3.40	15.20	0.04	26.00	29.20	4.89
CO_2						0.30	0.12	0.05	0.16	0.06
Undetermined	-1.62	0.91	4.31	-.04	5.05	1.56	0.40	-1.69	-2.23	0.45
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Fuel	80%/20% Wood/Wheat Straw Blend				Wheat Straw			Wheat Straw		
Fuel Ash	8.14%				7.95%			7.95%		

Und = undetermined. *Total fuel chlorine as % ash.

Figure 30 Relative element abundance, Superheater deposits, grate units (Jenkins et al., 1994)
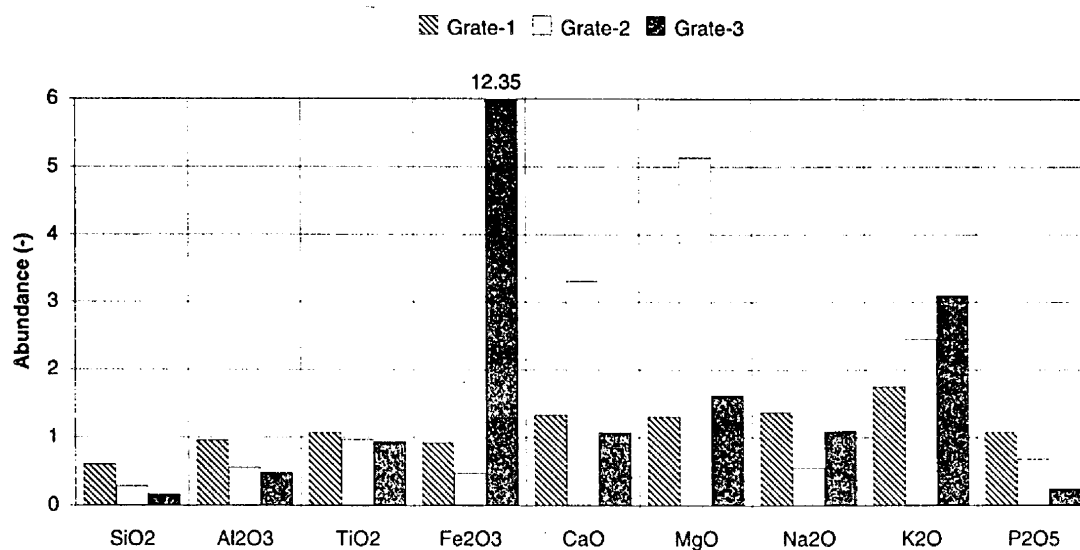
Figure 31 Relative element abundance:sulfur and chlorine, Superheater deposits, grate units (Jenkins et al., 1994
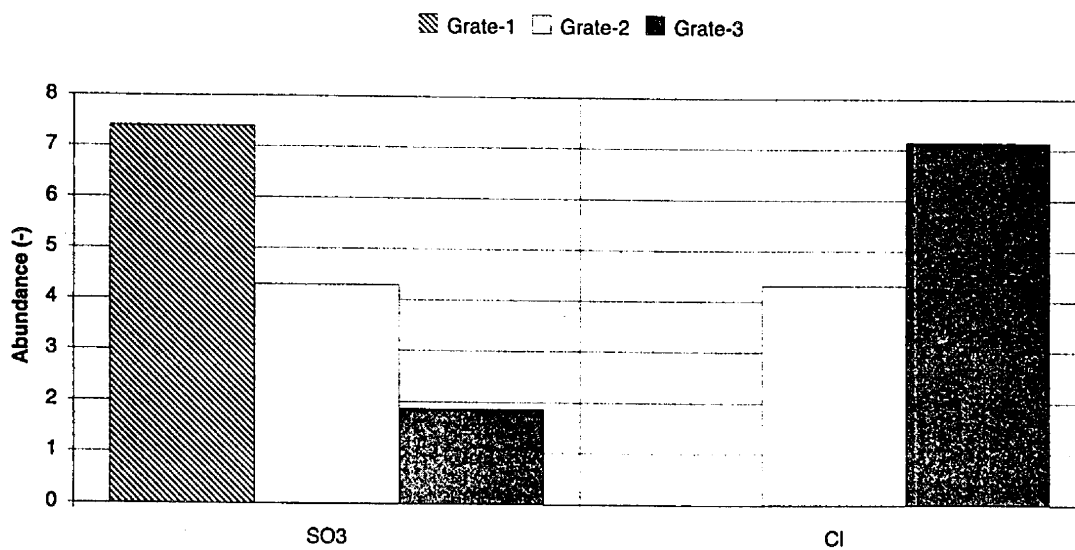
Figure 32 Superheater deposits from Wood-Straw Blend, Grate - 1
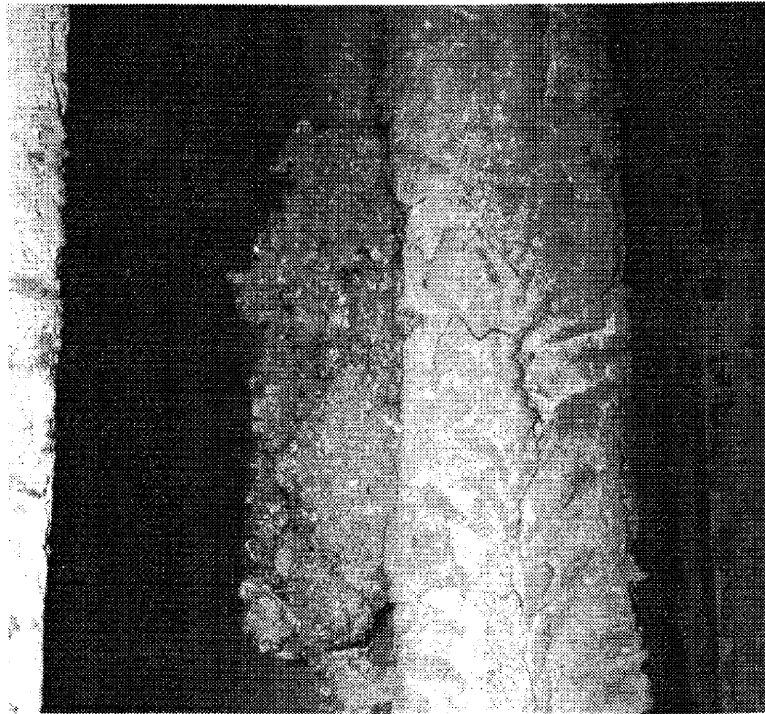
Figure 33 Superheater deposits from Wood-Straw Blend, Grate-1 (Oden, 1993)

Backscattered electron image of case and core of particles composed of identical low-melting flux-like material. Bonding material between particles is mostly alkali sulfate. X2000.
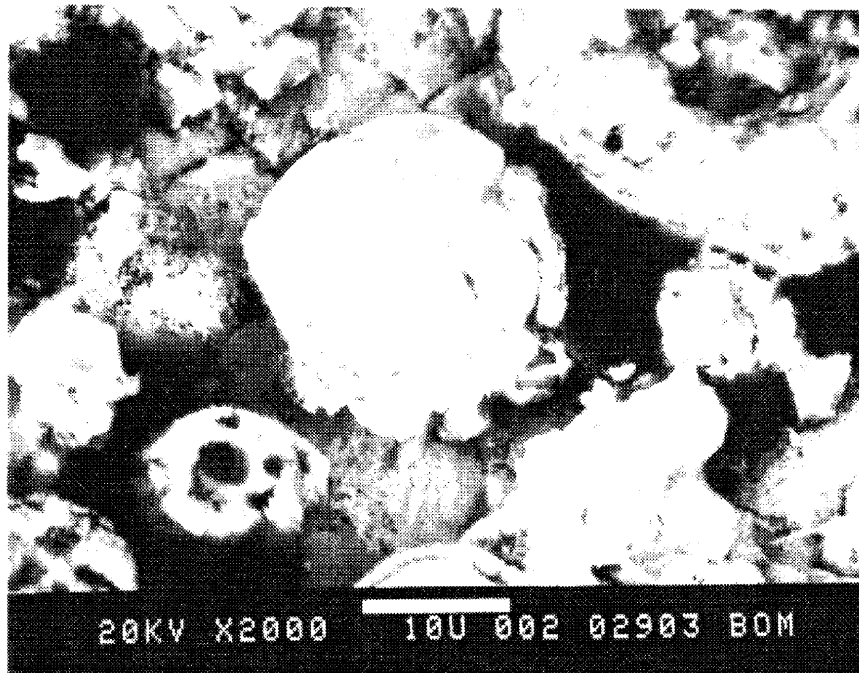
Figure 34 Grate ash agglomerate particle covered with bonding matrix. Note beads of
fused mineral. Wood-5% Imperial Straw Blend. Grate-1.
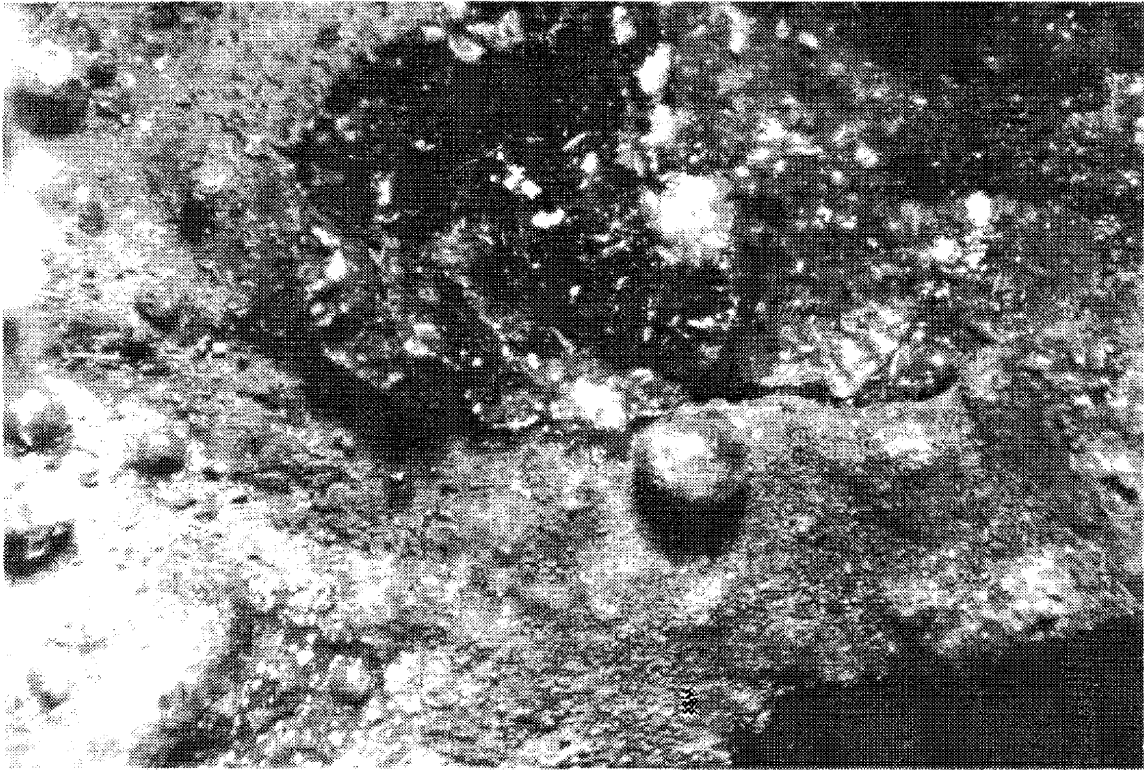
Figure 35 Backscatter image of bonding matrix Wood-Straw Blend, Grate-1. (a) siliceous
component, (b) intermediate phase (with 21% K_2O) embedded in (c)continuous glass
phase. (Hazen, 1993)
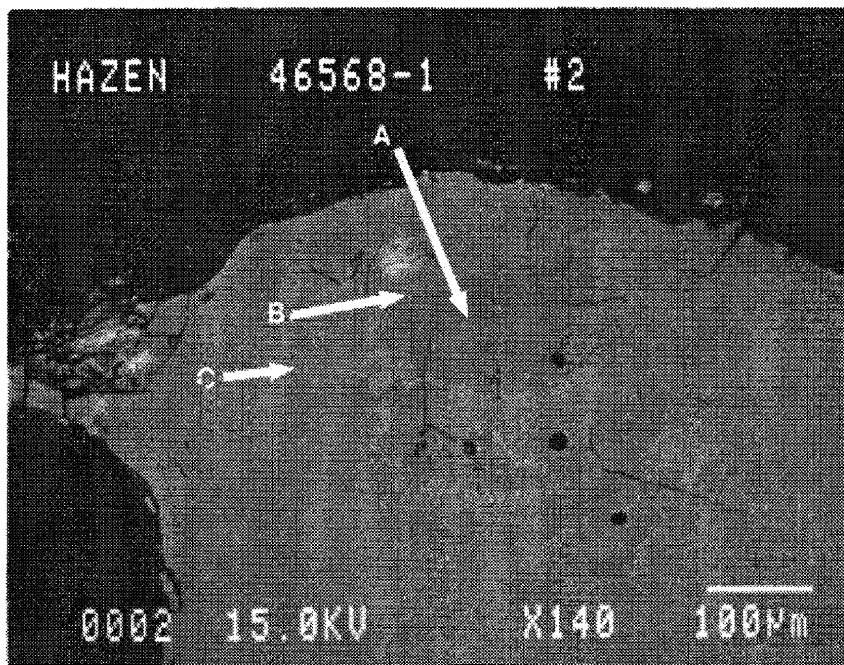
	A	B	C
SiO_2	64.20	54.60	58.60
Al_2O_3	26.20	24.00	12.70
TiO_2	.01	0.01	0.01
Fe_2O_3	.15	0.14	3.10
CaO	4.40	0.01	17.10
MgO	.01	0.01	3.40
K_2O	5.10	21.20	5.10
Total	100.07	99.97	100.01

Fluidized Beds

Deposits in the bubbling fluidized bed unit (FBC-1) were removed from the furnace wall above the expanded bed level, and from the screen tubes and superheaters in the horizontal convection pass after two months of operation. The heaviest fouling was found on the screen tubes, decreasing in severity downstream. The primary superheater (farthest downstream) was coated only with a light dust which was not readily sampled without contamination from tube metal. Both the screen tubes and the tertiary superheater had developed heavy deposits on the upstream side, with the characteristic aerodynamic wedge profile illustrated in Figure 4 (p.8) and Figure 36, following. The upstream deposits were more tenacious than the deposits on the back side of the tubes, in the wake region, which were finer textured and less tightly bonded.

Compositions of the deposits from FBC-1 are listed in Table 8 (p.51), with relative elemental abundance for the screen tubes and the tertiary and secondary superheaters shown in Figure 37 (p.50). The deposits on the screen tubes and superheaters for the most part show enrichment in potassium, sulfur, and chlorine relative to the fuel. The enrichment in chlorine and sulfate is of similar magnitude to the grate units. The deposits contain more calcium than the grate units, possibly as a result of higher fuel calcium concentrations and limestone injection.

The screen tube deposit composition from FBC-1 was not uniform throughout. Three different parts of the deposit were analyzed separately. The outer main wedge portion developing upstream into the oncoming flow, and representing the bulk of the deposit volume and mass, showed substantially more sulfation than either the deposit on the front (upstream side) of the tube at the surface, underneath the bulk deposit, or the back side deposit in the wake region of the tube (Table 8). The concentrations of carbonates (as CO_2) were higher in the back side deposit than on the front, whereas chlorine concentrations, like sulfur, were increased on the upstream side of the tubes at the surface. Cl was not as enriched in the outer wedge portion. This suggests the chloride stopped condensing as the deposit surface temperature increased with increasing deposit thickness and reduced heat transfer. Sulfation apparently continued, however. The total carbonate concentrations also increased downstream in the direction of cooler temperatures. The backside deposits from the tubes were depleted in potassium compared with the front surface. Calcium, as calcium carbonate, was the major species, with some increase in silica. Limestone addition to the bed appears to have coated the tubes initially, with little deposition occurring later in the wake region. The deposit sampled from the furnace wall, comprised of a sintered sandy agglomerate, was highly depleted in sulfur and chlorine, and greatly enriched in silicon, indicating a combination of fuel ash and bed media.

Mineralogical assays performed by Bureau of Mines using optical microscopy, X-ray diffraction, and scanning electron microscopy showed the primary phase in the bulk deposit on the tertiary superheaters to be KCl, with the primary phase on the downstream side of the secondary superheaters as $CaCO_3$. Secondary phases on the screen tubes consisted of calcium-silica-sulfates and potassium-calcium-sulfates. A number of other species were identified in minor or trace concentrations, including quartz, sodium chloride, and calcium phosphates.

Figure 36 Relative element abundance, Superheater deposits, fluidized bed units (Jenkins et. al, 1994)
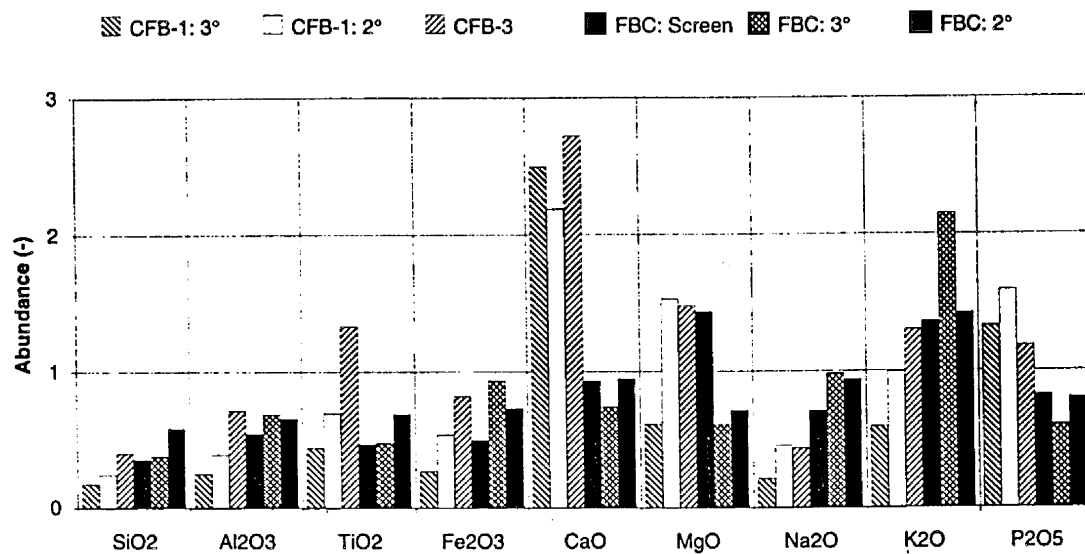
Figure 37 Relative element abundance, Superheater deposits, fluidized bed units (Jenkins et. al, 1994)
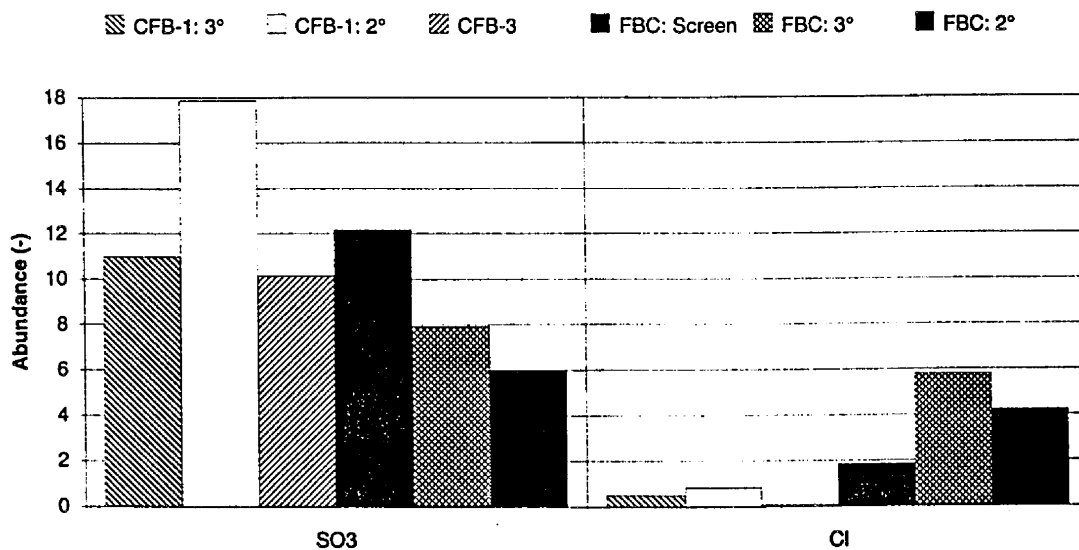
Table 8 Composition of Fuels and Deposits, bubbling fluidized bed boiler

	Fuel	Screen tubes	Screen, outer	Screen, front surface	Screen, back surface	3° Super-heater	2° Super-heater	2° Super-heater, front	2° Super-heater, back	Furnace wall
Ash Composition (% ash as oxide)										
SiO_2	28.27	10.27	9.43	16.70	19.52	11.01	16.78	14.53	23.79	62.76
Al_2O_3	8.28	4.62	4.57	4.09	6.67	5.86	5.53	3.76	5.85	11.49
TiO_2	0.84	0.40	0.32	0.30	0.67	0.41	0.59	0.54	0.72	0.53
Fe_2O_3	3.33	1.69	1.48	1.33	2.80	3.20	2.48	2.18	3.01	2.94
CaO	28.99	27.71	31.74	24.63	33.19	22.13	27.95	25.78	31.58	10.15
MgO	4.51	6.64	3.44	2.98	4.65	2.81	3.27	3.27	3.89	1.40
Na_2O	2.81	2.04	1.83	2.66	2.12	2.84	2.68	2.91	2.07	2.26
K_2O	9.58	13.40	13.20	19.20	7.85	21.20	13.90	17.20	5.78	4.72
SO_3	2.14	26.70	28.70	17.80	6.30	17.46	13.10	13.00	2.88	0.36
P_2O_5	2.95	2.48	2.35	2.09	2.62	1.82	2.40	2.33	2.41	0.74
Chlorine *	1.71	3.26	2.99	9.98	3.15	10.20	7.37	9.74	1.76	0.13
CO_2	4.98	1.60	1.40	5.30	8.70	2.20	4.10	4.90	14.00	.30
Undetermined	1.61	-0.81	-1.45	-7.66	1.76	-1.14	-0.15	-0.14	2.26	2.22
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Fuel	60% 37% 3%	urban wood orchard almond shell								
Fuel Ash	2.30%									

Und = undetermined. *Total fuel chlorine as % ash.

Deposit compositions for the three circulating fluidized beds are listed in Table 9, (p.53 following) The trends for all three are similar, but instead of the superheater deposits being enriched in potassium, calcium is the more prominent species. The compositions indicate in all three cases that the formation of calcium sulfate is an important characteristic with these units, possibly due to the addition of limestone to the bed, except for CFB-3 which did not add limestone. None of the CFB deposits showed enrichment in chlorine. The fuels used in the CFB units were lower in chlorine than in the grate units or FBC-1. The carbonate concentrations of the tertiary superheater deposits for CFB-1 (Figure 9, p.13) were high, but low for CFB-2, possibly as a result of the differences in the lime or limestone addition. The fuel calcium concentrations cannot be directly compared because only water-soluble calcium was analyzed for CFB-2, and little of the calcium is water soluble (Baxter, et al., 1993). A deposit removed from the wall of the cyclone vortex finder in CFB-1 is similar in composition to the superheater deposits, revealing the presence of calcium sulfate. A deposit removed from the bed of the same unit appears to be dominated in composition by the bed media.

For CFB-2, the primary crystalline phase on the fireside of the tertiary superheater deposit was a potassium-calcium sulfate, while farther into the deposit, nearer the tube surface, the primary phase consisted of calcium-magnesium- or calcium-aluminum silicates. Secondary and minor phases in the deposits were also comprised of complex silicates, including feldspars, consistent with the deposition of soil and media particles by impaction, and of phosphates. Chlorides were not identified. The primary phase in the superheater deposit of CFB-3 was calcium sulfate, with a minor phase of a potassium calcium sulfate and trace amounts of calcium phosphates and calcium-magnesium silicates. These results are consistent with the reduced importance of condensation as the deposit thickness and surface temperature increase. With reduced condensation, sulfation would become dominant.

Table 9 Composition of Fuels and Deposits, circulating fluidized bed boilers

	CFB-1									CFB-2				CFB-3		
	Fuel	Screen tubes	3° Super-heater	3° Super-heater	3° Super-heater	2° Super-heater	Cyclone	Bed Deposit	Spent Media	Fuel φ	3° Super-heater	2° Super-heater	1° Super-heater	Fuel	Fresh Media	Super-heater
Ash %																
SiO2	48.35	64.35	9.05	3.87	9.08	12.01	4.31	71.12	69.13		12.80	11.78	13.88	52.55	82.24	20.17
Al2O3	11.11	11.18	2.78	2.21	3.00	4.42	2.43	10.23	10.73		6.15	6.52	6.63	13.15	9.99	9.02
TiO2	0.51	0.31	0.28	0.12	0.24	0.36	0.09	0.28	0.36		0.56	0.51	0.58	0.43	0.21	0.55
Fe2O3	4.17	1.58	1.74	0.80	1.21	2.27	0.86	1.51	1.95		3.89	1.14	4.29	8.18	1.56	6.45
CaO	17.48	12.02	34.90	50.44	46.95	38.99	51.03	9.28	9.47	1.34	25.50	23.28	22.84	10.06	2.33	26.29
MgO	3.77	1.27	8.65	3.33	2.47	5.89	6.26	1.10	0.64		5.96	6.66	6.10	3.27	0.40	4.65
Na2O	2.56	2.28	0.80	0.30	0.59	1.18	0.12	1.94	2.02	0.98	3.32	4.53	4.44	5.90	2.23	2.47
K2O	6.90	5.66	5.70	2.63	4.37	7.01	0.31	4.78	4.58	2.44	9.41	9.99	9.31	5.04	3.10	6.31
SO3	1.38	0.16	23.80	12.90	16.30	25.10	34.80	0.21	0.48	3.57	29.70	28.10	26.40	2.10	0.22	20.30
P2O5	1.49	0.58	2.25	1.75	2.13	2.42	1.79	0.46	0.48		2.65	2.76	2.78	1.90	0.01	2.16
Cl	.39	0.04	0.22	0.08	0.21	0.33	0.01	0.01	0.02	0.63	0.01	0.21	0.47	0.58	0.01	0.05
CO2			9.58	22.24	19.03						0.15	0.11	0.17			
Undet	1.89	0.57	0.25	-0.67	-5.58	0.02	-2.01	-0.92	0.14		-0.10	4.41	2.11	-3.16	-2.30	1.58
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		100.00	100.00	100.00	100.00	100.00	100.0
Fuel	47% urban wood 47% orchard 6% almond shell blend									Wood/ Pits variable blend				80% 20%	Wood Pits, shells, hulls	
Fuel Ash	7.70%									5.32%				5.13%		

Und = undetermined. *Total fuel chlorine as % ash. φ based on weekly composite samples, includes water soluble K, Na, and Ca only.

Laboratory experiments:

Compositions for fuel ash, probe deposits, and flyash from seven laboratory combustion experiments are reported in Tables 10 through 12.

Straws and grass

Rice straw combines high chlorine with a high silica fuel ash (Table 10). Two tests with rice straw were conducted, the second of which, as indicated previously, was terminated early due to tube deposit attrition from loose furnace wall deposits. The rotating horizontal probe only was used for these tests. The deposit on this tube formed initially as a uniform white layer, a universal characteristic of the laboratory experiments. Subsequently, the deposit grew as a porous sintered matrix, which was readily brushed from the tube at the end of the experiment. The outer deposit layer from the second test was somewhat enriched in potassium and depleted in silicon compared to the bulk probe deposit from the first test. All deposits were depleted in sulfur compared to the fuel.

Heavy deposits formed on the wall of the furnace below the fuel injection point. Samples were recovered both during the experiment and after cooling and cleaning the furnace. The wall deposits were highly porous with a sintered sponge-like appearance, white in color where they were attached to the wall, and dark (shading from purple to black) extending away from the wall. The white and dark portions were analyzed separately. The white portion was enriched in aluminum, titanium, and iron compared to the dark deposit, which may be due to the influence of the furnace wall material, a mullite ($3Al_2O_3 \bullet 2SiO_2$) ceramic, and possible contamination from residual coal ash deposited on the wall in the tests previous to this experiment. The flyash was also enriched in aluminum, titanium, and iron, as well as potassium. The absolute amounts are small and do not suggest substantial contamination. The flyash also has a high undetermined fraction, which may account in part for the enrichment ratios observed. Alternatively, the undetermined fraction may include chlorine or carbon.

Regardless, the probe deposit has a composition very similar to the composition of the fuel ash.

X-ray analysis during scanning of the wall deposits with SEM did not detect chlorine. SEM analyses of probe deposits did show evidence of chlorine, but quantitative concentrations were not obtained. The rice straw wall deposits show distinctly a glassy matrix in which lie imbedded porous silica particles. These particles are nearly pure silicon (94%) with potassium making up most of the residual, and almost certainly derive directly from the fuel. The glassy phase binding the silica particles is 64% silicon, with 19% potassium, and smaller amounts of calcium, magnesium, sodium and other elements (Baxter, et al., 1993). The glass appears to have formed over time by reaction of silica with potassium vapor and other elements to form a low melting point silicate. Figure 38. The bulk composition of the glass is consistent with a melting point between 900° and 1200° C at equilibrium (Levin, et al., 1964). The liquidus surface is steep in the region of this composition, and the observation of a molten phase is consistent with the

possible range in furnace gas temperatures. Relative concentrations of chlorine show the layer of the probe deposit next to the tube surface to be chlorine enriched relative to the outer deposit layer. Potassium and sulfur are also enriched in the inner layer, while silicon is depleted.

Figure 38 Wall and tube deposits from MFC tests show that porous silica nodules in rice straw absorb and react with potassium vapor to form a low melting point silicate..
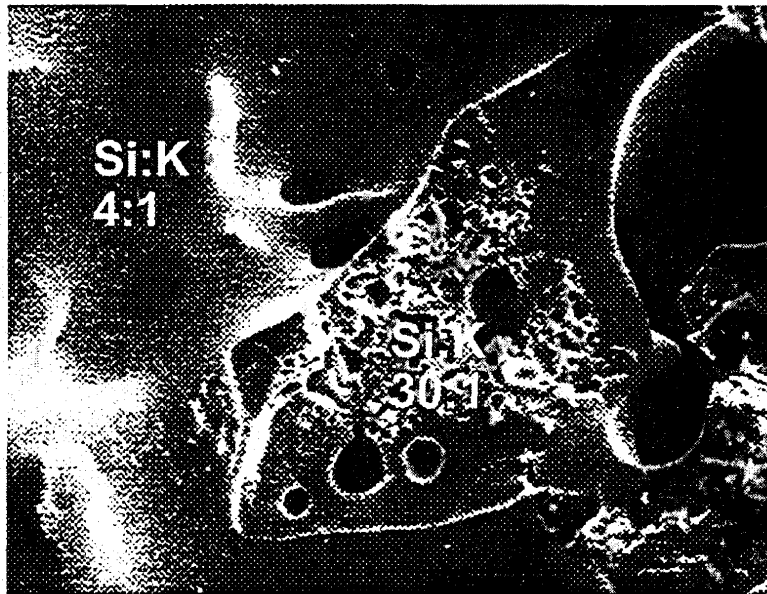
The wheat straw deposits are in many respects similar to the rice straw deposits. Two tests were conducted without hindrance from dislodged wall deposits. The fuel chlorine concentration of the wheat straw was about 40% that of the rice straw fuel, but wheat straw is also a high chlorine, high silica fuel. Chlorine concentrations in wheat straw have often been observed at substantially higher levels. The vertical waterwall probe was used along with the rotating horizontal probe. The deposits collected were segregated into different parts for analysis. During the second test, the horizontal probe rotation was stopped and the deposit collected with the probe stationary. The deposit built up in three distinct layers beginning with a uniform fine textured white deposit next to the probe surface, a more porous intermediate layer which was brushed from the tube, and an upper crown deposit with the appearance of sintered fuel ash particles. The latter portion of the deposit was only loosely bonded and was removed simply by inverting the tube. Various types of deposit were collected from the waterwall probe. On the upper horizontal surfaces of this probe, deposits were formed which were similar in character to the crown deposit on the horizontal probe. These varied in hardness and color. On the vertical face of the waterwall, a fine textured white layer formed next to the surface, followed by a darker layer building outward, but considerably finer textured than any of the crown deposits. The compositions of the deposits, including one removed from the furnace wall, are listed along with the fuel and flyash compositions in Table 12.

Silicon was the major species in all samples. The inner deposit layers from both probes were depleted in silicon relative to the outer layers. Potassium enrichment was evident in all of the deposit samples as well as the fly ash. The deposit layers showed increasing potassium and sulfur concentrations moving inward towards the probe surfaces, although sulfur was depleted relative to the fuel. SEM/X-ray analyses gave qualitatively higher chlorine concentrations in the inner layers as well, although no quantitative determinations for chlorine were made. Phosphorus was enriched in the outer deposit layers compared to the inner layers, and was enriched in the fly ash as well. Furnace wall deposits did not show any evidence of contamination as with rice straw. The iron enrichment in the inner layers of the waterwall deposit may have been the result of tube metal contamination when sampling, however.

Results for switchgrass are given in Table 11. Two tests were completed, the rotating horizontal probe results are shown for both. The waterwall probe and a stationary probe were utilized during one of the tests. Switchgrass, like the straws, contains high concentrations of chlorine and silicon, although its total ash content is only one quarter that of rice straw. The Ca concentration was higher than rice or wheat straw ash by a factor of 3 to 4, although this may be due to the inclusion of adventitious materials (soil), suggested by the high aluminum concentration. The presence of aluminum in quantity is typically an indicator of soil contamination because aluminum in plants is normally present at low levels.

Deposit compositions from switchgrass were in many respects similar to those from the straws, although the deposits were not segregated in the same way as for wheat straw. All contained high concentrations of silica in combination with potassium. The sulfate enrichment in the switchgrass deposits was substantially greater, however, when contrasted with the straw deposits, even though switchgrass has a sulfur concentration about one quarter that of wheat straw and roughly the same as rice straw. The sulfur enrichment was highest in the stationary horizontal probe deposit. This deposit also had the greatest potassium enrichment, nearly four times the level of the fuel ash, which in combination with the sulfur implies the presence of an alkali sulfate. The fly ash was somewhat depleted in silicon, but the undetermined fraction was high for this sample, possibly as a result of undetermined carbon. Normalizing the silica concentration in the flyash to the total determined species yields a silica concentration of roughly 60%. The deposit collected from the top of the waterwall was not enriched in sulfur as was the stationary probe deposit, possibly indicating the instability of the potassium sulfate at furnace temperature. The furnace wall deposit, like the wall deposits from straw, was greatly depleted in sulfur.

Table 10 Inorganic Compositions (% as oxide), MFC test on rice straw

	Fuel ash	Flyash (2)	Furnace wall, black (2)	Furnace wall white (2)	Probe outer layer (2)	Probe, rotating (1)
Ash Composition (% ash as oxide)						
SiO_2	80.15	58.59	79.01	73.50	67.02	76.57
Al_2O_3	1.46	2.65	1.13	9.56	2.10	0.70
TiO_2	0.06	0.13	0.04	0.47	0.23	0.04
Fe_2O_3	0.85	1.56	0.79	6.87	1.18	0.92
CaO	2.03	2.07	4.56	2.28	3.73	2.12
MgO	2.11	1.93	1.04	1.41	1.60	1.45
Na_2O	0.91	0.88	0.70	0.67	0.68	0.41
K_2O	8.51	17.63	12.20	5.19	14.60	9.65
SO_3	1.22	1.10	0.03	0.14	0.67	0.82
P_2O_5	1.68	1.64	1.54	0.65	4.56	1.16
Und.	1.02	11.82	-1.04	-0.74	3.59	6.16
Total	100.00	100.00	100.00	100.00	100.00	100.00

Test number indicated in parentheses. Und = undetermined.

Table 11 Inorganic Compositions (% as oxide), MFC test on switch grass

	Fuel ash	Flyash (1)	Furnace wall, (1)	Probe, rotating (1)	Probe rotating (2)	Probe, stationary (1)	Water wall (1)	Water wall (2)
Ash Composition (% ash as oxide)								
SiO_2	69.51	47.91	68.85	42.42	53.92	32.35	63.70	55.17
Al_2O_3	3.84	6.60	3.58	3.88	5.45	3.02	5.70	6.18
TiO_2	0.14	0.34	0.21	0.22	0.33	0.19	0.34	0.34
Fe_2O_3	1.52	2.00	1.52	14.72	3.31	7.13	3.60	3.54
CaO	8.17	7.70	9.10	6.85	8.16	6.25	9.99	10.05
MgO	3.48	2.66	3.76	2.62	3.10	2.39	3.57	3.30
Na_2O	0.82	0.82	0.46	0.74	0.59	1.25	0.64	0.75
K_2O	7.26	7.39	9.07	11.85	14.10	25.52	7.59	9.33
SO_3	1.49	1.58	0.37	3.87	2.72	8.94	1.15	3.96
P_2O_5	3.63	2.76	3.58	3.12	3.64	3.64	3.08	2.91
Und.	0.14	20.18	-0.50	9.71	4.68	9.32	0.64	4.47
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Test number indicated in parentheses. Und = undetermined.

Table 12 Inorganic compositions (% as oxide), MFC test on wheat straw.

	Fuel ash	Flyash (2)	Furnace wall (2)	Probe stationary crown (20	Probe, stationary inner layer (2)	Probe, stationary intermediate (2)	Water wall, crown (1)	Water wall, crown brown (2)	Water wall, crown hard black (2)	Water wall, crown soft black (2)	Water wall, inner white layer (2)	Water wall, inner white layer (1)	Water wall, outer dark layer (1)	Water wall, outer layer (2)
Ash %														
SiO_2	67.54	50.49	66.28	58.90	49.92	57.13	56.82	67.46	53.92	61.04	43.49	41.60	50.68	52.85
Al_2O_3	2.14	1.35	1.26	2.08	2.78	3.01	1.36	2.46	5.45	2.40	1.63	2.00	1.50	1.44
TiO_2	0.10	0.04	0.11	0.04	0.14	0.15	0.08	0.14	0.33	0.08	0.08	0.12	0.15	0.08
Fe_2O_3	1.22	1.40	0.99	1.18	1.48	1.32	0.90	1.30	3.31	1.16	2.86	4.27	1.30	1.42
CaO	3.08	5.28	4.48	4.85	4.30	5.74	2.70	3.52	8.16	4.67	2.89	3.06	4.65	5.03
MgO	2.88	1.10	2.67	2.40	4.07	3.04	2.49	3.15	3.10	1.73	2.55	2.55	1.60	1.86
Na_2O	2.05	1.09	0.90	0.86	1.20	1.01	0.67	0.87	0.59	0.86	0.83	0.95	0.87	0.90
K_2O	14.38	23.10	18.40	19.50	24.80	21.10	19.80	16.14	14.10	19.30	27.50	28.40	23.90	24.20
SO_3	1.41	5.77	1.23	1.59	4.39	2.04	2.28	2.61	2.72	1.38	6.37	7.37	3.44	3.11
P_2O_5	5.02	3.35	2.16	4.51	2.02	3.79	1.23	1.57	3.64	3.48	1.34	1.28	3.75	3.77
Undet.	0.18	7.03	1.52	4.09	4.86	1.67	11.67	0.78	4.68	3.90	10.46	8.40	8.16	5.34
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Test number indicated in parentheses. Und = undetermined.

Shells, hulls, pits:

Fuel ash, fly ash, and deposit compositions from an MFC test with almond shells are listed in Table 13. Almond shells, as with almond hulls, are distinctive in their high potassium concentrations in the ash (Table 14). K_2O accounted for almost half the fuel ash. Unlike the straws and grass, the silica concentration in almond shell ash was low, about 10%. Calcium and phosphorus were the other major constituents of shell ash. The chlorine concentration was low at 0.03% of dry fuel, whereas the ash sulfate concentration was not substantially different from rice straw or switchgrass.

Two tests with almond shells were conducted using all three probes. Flyash samples were segregated into coarse particles collected loose in the filter holder and representing partially reacted fuel particles, and a fine fraction collected on the filter. The analytical results were combined on the basis of the respective sample weights to give an average flyash composition. Loose particles were also collected on the horizontal surfaces of the waterwall probe, and a lightly sintered deposit formed on the top of this probe. The undetermined fractions were very high in almost all cases, almost certainly as the result of large amounts of unburned carbon. Based on the determined fraction only, the silica concentration of the coarse flyash was in excess of 30%. The coarse particles collected on the waterwall probe, as well as the crown deposit collected on this probe, also showed elevated silica concentrations. Sulfate in the fine flyash fraction was enriched over that in the coarse flyash fraction, possibly due to sulfate condensing on the filter.

The initial deposits were gray-white in color, but brightened over time, and all were fine textured. A few partially burned carbon-containing fuel particles adhered to the deposit after impact, and may account for some of the undetermined fraction in these deposits. The deposit potassium and sulfur concentrations were not particularly enriched relative to the fuel, and potassium continued to make up the majority of the deposit mass. Ca, Mg, Na, and P were all depleted in the deposits relative to the fuel. The mass ratio of K_2O to SO_3 is consistently on the order of 20, and well in excess of the equivalent mass ratio for potassium sulfate (2.35). The contribution from chlorine in this case is unknown, but is in insufficient concentration in the fuel to account for the residual potassium as KCl. In the absence of sufficient sulfur and chlorine, the potassium may have deposited as an hydroxide or carbonate.The crown deposit on the waterwall probe was quite similar in composition to the fuel ash.

The characteristics of the almond hull deposits (Table 14) were similar to those for almond shell. Potassium accounted for more than half the fuel ash, with total ash and chlorine concentrations twice those for shell. The initial deposit was again gray-white in color, indicating the presence of carbon, but brightened to a brilliant white after approximately 3 hours and remained so for the remainder of the experiment. The deposit was fine textured throughout, with a superficial coating of partially reacted fuel particles sticking after impact. The deposit enrichment ratios for potassium and sulfur were quite similar to those for almond shell, again suggesting the presence of potassium hydroxide or carbonate on the probe surfaces. The flyash collected on the filter surface showed a distinct segregation by color and texture, with the center portion having a brighter tint and flake-like appearance compared to the gray, powdery outer deposit. The outer

portion had substantially higher silica and iron concentrations, but a lower undetermined fraction suggesting unreacted carbon was not the reason for the difference in color.

Potassium compounds from almond hulls were typical bonding agents between silica or media particles in superheater deposits. In some cases the potassium reacted with the silica to form a bonding glass. Figure 39 is an SEM photo of three particles of fluidized bed sand that cemented together with a glass containing 6% K_2O (Table 17) when burning a blend of 15% almond hulls and 85% urban wood waste in CFB-1.

Olive pits had a uniquely high sodium concentration as a result of the olive processing. Pits had moderate chlorine (0.08%), and a low total ash content (Table 15). The silica concentration in the ash was also moderate, but the potassium concentration was very low, likely as a result of leaching during processing. The deposit and flyash compositions are included in Table 15. The deposits were enriched in both potassium and sulfur, and depleted in sodium compared to the fuel. All analyses had high undetermined fractions, again the likely result of undetermined carbon. Sodium, although somewhat depleted relative to the fuel, was still the predominant alkali species present in the deposits. The total sulfur and chlorine in the fuel would account for roughly 30% of fuel sodium if present as sulfate and chloride, again suggesting the possible presence of hydroxides or carbonates.

Commercial wood and shell blend

The results for the commercial wood and almond shell blend are listed in Table 16. This fuel had high silicon and aluminum concentrations due to the inclusion of soil contaminants, which is typical for power plant fuels of this type. The chlorine concentration was quite low at 0.03%. The fuel had a moderate total ash content, with low alkali and moderate calcium concentrations.

A visible deposit developed within 2 min after starting, white in color, fine textured, and sticky. Larger particles could be seen to adhere to it after impact. The color darkened somewhat over the course of the test, developing a grayish cast, but the deposit thickness did not develop as fast as with straw and the deposit remained fine textured. Relative to the fuel, the deposit composition showed little enrichment except in potassium and sulfur. The greatest enrichment occurred on the stationary horizontal probe, and an intermediate enrichment on the vertical face of the waterwall probe. Partially burned fuel particles collected loose on the waterwall were depleted in sulfur, but the flyash overall contained sulfur. The ratio $(CaO+Na_2O+K_2O)/SO_3$ in the deposits is generally consistent with the deposition of these elements as sulfates, particularly in the case of the stationary horizontal probe.

Table 13 Inorganic compositions (% as oxide), MFC test on almond shell.

	Fuel ash	Coarse Flyash	Fine Flyash	Combined Flyash	Probe, stationary (1)	Probe, stationary (2)	Probe, rotating (1)	Probe, rotating (2)	Water wall, crown (2)	Water wall, loose particles (2)	Water wall, loose particles back (2)	Water wall, surface (1)	Water wall, surface (2)
Ash %													
SiO_2	9.82	4.15	14.11	6.14	6.61	2.72	4.24	5.06	11.75	12.73	20.97	5.82	3.18
Al_2O_3	2.44	0.93	6.93	2.13	1.82	0.76	1.10	1.27	3.76	3.32	4.93	1.53	1.04
TiO_2	0.10	0.03	0.37	0.10	0.11	0.06	0.05	0.07	0.16	.17	0.24	0.07	0.06
Fe_2O_3	2.46	0.34	2.27	0.73	6.92	1.15	1.70	2.00	3.46	3.91	2.91	6.02	2.80
CaO	11.95	1.07	4.85	1.83	4.97	3.19	3.88	4.22	11.87	8.76	7.53	7.49	5.85
MgO	4.35	0.25	1.72	0.54	1.85	1.28	1.47	1.69	4.43	3.42	2.49	2.58	2.04
Na_2O	1.61	0.23	0.85	0.35	0.69	0.83	0.75	0.93	1.11	0.85	0.94	0.69	0.86
K_2O	44.72	5.91	30.04	10.74	34.92	53.92	46.07	53.46	33.63	32.61	21.37	35.64	50.40
SO_3	1.41	0.10	2.56	0.59	1.86	1.94	2.16	1.91	1.36	0.75	0.74	2.43	2.41
P_2O_5	6.52	0.30	2.11	0.66	2.78	2.17	2.36	2.85	6.29	4.77	2.92	3.59	3.03
Undet.	14.63	86.70	34.22	76.20	37.47	31.98	36.22	26.54	22.18	28.71	34.96	34.14	28.33
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Test number indicated in parentheses. Und = undetermined.

Table 14 Inorganic compositions (% as oxide), MFC test on almond hull.

	Fuel ash	Coarse Flyash	Fine Flyash outer filter grey	Fine Flyash, outer filter grey	Probe, stationary	Probe, rotating	Water wall, loose particles	Water wall, surface
Ash %								
SiO_2	6.03	1.39	8.27	23.15	2.33	2.97	12.28	3.68
Al_2O_3	1.28	0.37	4.32	12.06	0.65	0.77	4.29	1.27
TiO_2	0.07	0.02	0.21	0.58	0.05	0.05	0.28	0.08
Fe_2O_3	0.83	0.15	0.93	2.71	0.42	1.26	1.88	1.44
CaO	8.66	1.23	3.17	3.42	2.34	2.61	9.24	4.71
MgO	5.01	0.66	1.78	1.84	1.36	1.45	4.63	2.46
Na_2O	0.99	0.12	0.61	0.74	0.64	0.54	0.63	0.85
K_2O	53.60	14.48	36.47	23.65	56.47	43.75	37.98	52.55
SO_3	1.46	0.16	1.99	1.54	1.84	1.43	1.30	2.50
P_2O_5	7.33	1.06	2.62	2.19	2.12	2.25	6.43	3.82
Undet.	14.74	80.36	39.63	28.12	31.78	42.92	21.06	26.64
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Test number indicated in parentheses. Und = undetermined.

Table 15 Inorganic Compositions (% as oxide), MFC test on olive pits

	Fuel ash	Flyash	Probe rotating	Probe, stationary	Water wall
Ash Composition (% as oxide)					
SiO_2	31.47	4.12	13.14	18.78	32.62
Al_2O_3	6.45	2.62	3.16	4.56	6.59
TiO_2	0.31	0.16	0.17	0.23	0.33
Fe_2O_3	6.97	1.76	12.37	13.93	11.09
CaO	13.66	5.25	8.15	10.06	6.69
MgO	4.48	1.15	2.68	3.23	2.09
Na_2O	27.43	2.54	21.20	18.25	11.29
K_2O	1.77	0.64	7.31	5.73	4.46
SO_3	1.98	1.53	7.36	5.91	4.07
P_2O_5	3.34	0.50	2.73	3.20	1.24
Undetermined	2.12	79.73	21.73	16.12	19.53
Total	100.00	100.00	100.00	100.00	100.00

Und = undetermined.

Table 16 Inorganic Compositions (% as oxide), MFC test on wood/shell blend.

	Fuel ash	Flyash	Probe stationary	Probe, rotating	Waterwall surface	Waterwall loose particles
Ash Composition (% as oxide)						
SiO_2	55.69	35.61	42.88	50.56	42.79	63.44
Al_2O_3	10.75	11.97	9.54	11.19	9.90	12.05
TiO_2	.52	0.63	0.49	0.53	0.44	0.54
Fe_2O_3	4.72	3.86	7.68	8.34	4.30	4.13
CaO	14.04	10.49	11.97	10.10	16.09	8.33
MgO	3.01	2.03	3.02	2.83	3.29	1.86
Na_2O	2.17	1.51	2.48	2.69	2.40	2.56
K_2O	4.39	5.73	11.40	7.87	9.83	3.92
SO_3	1.11	1.68	6.29	3.76	4.56	0.45
P_2O_5	1.54	0.99	1.94	1.67	1.96	0.71
Undetermined	2.06	25.50	2.31	0.46	4.44	2.01
Total	100.00	100.00	100.00	100.00	100.00	100.00

Und = undetermined.

Table 17 Inorganic Composition (% as oxide), CFB cyclone deposit from 85% wood/15% almond shell blend in Figure 39 and bonding material for adjacent particles. CFB-1.

	Average many particles	Grain left side No. 21a	Grain right side No.21a	Bonding material No. 21a	Bonding Material No. 21b	Bonding Material No. 23
Composition (% elements analyzed)*						
SiO_2	57.5	55.2	99+	74.3	52.0	51.0
Al_2O_3	12.3	1.7	<1	11.6	17.8	10.5
TiO_2	1.3	0.8	<1	0.7	<1	1.1
Fe_2O_3	6.4	4.8	<1	2.1	3.6	3.8
CaO	12.0	28.3	<1	1.8	<1	12.0
MgO	3.6	4.7	<1	0.5	<1	4.5
Na_2O	2.9	1.1	<1	3.0	<1	2.3
K_2O	4.1	3.6	<1	6.1	26.7	7.1
Total	100.0	100.0	100.0	100.0	100.0	100.0

SEM by MEI, Inc. for T.R. Miles. *Note: not analyzed for chlorine, sulfur or phosphorus.

Figure 39 Fluidized bed media particles fused with high and variable potassium matrix from burning 15% almond shells with 85% urban wood waste in circulating fluidized bed. 200X (CFB-1)
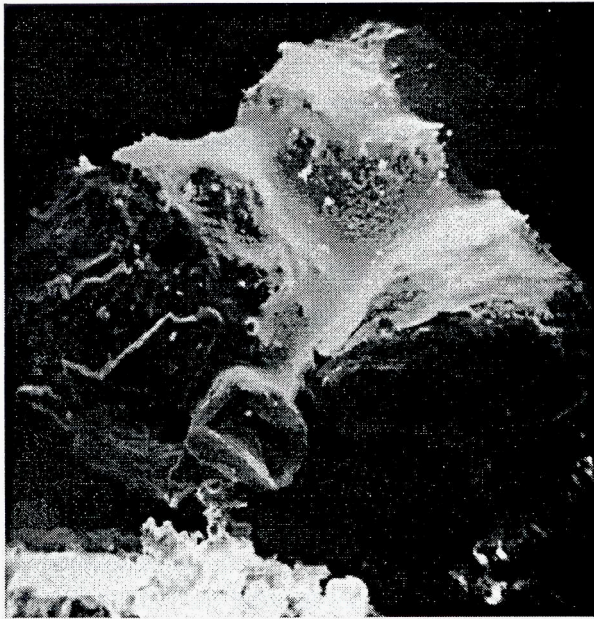
Discussion

Boiler deposits form in a complex interplay of elements from the fuel, additives, bed media, and the boiler structures themselves. The results of the full-scale and laboratory tests show distinctively the influences of fuel composition, limestone addition, and fluidized bed media. The stoker fired unit (Grate-1) burning a blend of wood with straw and the bubbling fluidized bed (FBC-1) burning wood and shell developed superheater deposits enriched in potassium and sulfate. Superheater deposits from the latter facility were also enriched in chlorine and carbonate. The concentrations of sulfates, chlorides and carbonates vary along the convection pass in a manner apparently consistent with the stability of the compounds; that is, as the temperature increases, the alkali species decompose in the order of carbonates, sulfates, and chlorides. The grate units firing straw produced superheater deposits enriched in potassium and chlorine, with lower concentrations of sulfates and carbonates. The fluidized beds are distinctive for the production of superheater deposits enriched not in potassium, but in calcium, as calcium sulfates. The calcium enrichment is probably related to the addition of limestone or lime to the bed during operation, but one unit not adding limestone also had deposits enriched in calcium sulfate. The superheater deposits from the bubbling fluidized bed had much higher concentrations of chlorides than did those from the circulating fluidized beds, which may be related to differences in fuel composition but it is also indicative of differences due to recirculation. Grate and bed deposits were dominated in composition by fuel ash and media, with loss of volatile sulfur, as in the case of the MFC furnace wall deposits.

The laboratory experiments reveal the influences of fuel composition and structure. Probe deposits from straw were enriched in potassium and chorine next to the probe surface, developing outwards into a matrix of sintered silicate-rich flyash particles. Switchgrass deposits also showed potassium enrichment, and greater enrichment in sulfate compared to the straws. The high potassium almond shells and hulls formed fine textured deposits, rich in potassium and suggesting the deposition of hydroxides or carbonates. A similar result was obtained for olive pits, high in sodium rather than potassium, and again suggesting sodium depositing as other species in addition to sulfates and chlorides. The deposits formed from the commercial wood and almond shell blend were potassium and sulfate enriched, as in the full-scale deposits, but contained more silicon and less calcium. Greater direct flyash capture and the lack of calcium from limestone probably account for the differences in the laboratory and full-scale deposit compositions in the latter case. Differences in combustion and flow regimes between the laboratory multi-fuel combustor and the full-scale circulating fluidized bed are possibly also responsible, but the initial deposition of alkali sulfate species appears consistent between model and full-scale facilities.

The manner in which fuel elements and elements from other sources become incorporated into deposits on boiler heat transfer surfaces is not entirely understood, but physical mechanisms and conceptual chemical pathways have been developed. A highly simplified and abbreviated conceptual scheme for various chemical interactions among major biomass fuel elements appears in Figure 40. Several possible routes are illustrated for the alkali metal, potassium, and the alkaline earth metal, calcium, to deposit on a surface. The species shown appear to account for much of the superheater deposit mass identified in the full-scale experiments. Other elements, such as sodium or magnesium, may follow generally similar pathways. Not shown in the figure are all the physical conditions, which greatly influence the deposit composition and properties.

Figure 40 Transformation of Mineral Matter in Biomass (Bryers, 1994).

Convective Heat Transfer Surface

Low Temp.

Heterogeneous
Condensation
KCl,NaCl

NaCl
KCl
K₂SO₄

Diffusion

Release of
Volatile
Inorganic Vapor
(K,P,Ca,Cl)

Oxidation
Chlorination
Sulfidation
K₂O,KOH,CaO,P₂O₅,HCl

Homogeneous
Condensation,
Nucleation,
Coalesence

Combustion

K₂SO₄

SIO₂,CaO,MgO
Na₂O Fe₂O₃

Cl

NaCl

K₂SO₄

Cl,K,S

Scavenging
Agglomeration

Molten Fly Ash
SIO₂,(NaCa)(AlSi)₄O₈

Reentrainment

Inertial
Impact

Viscous Slag

Molten Layer

Low Viscosity
High Fluid Temp.

Fly Ash

High Surface
Temperature

Radiant
Heat Transfer
Surface

Low Surface
Temperature

High Temp.

Convective Heat Transfer Surface

Potassium can exist in the original biomass in different forms, including ionic and organometallic forms, and salts. For all biomass it is atomically dispersed in the fuel, unless present through contamination. By contrast, silicon occurs primarily as hydrated silica grains. Upon combustion, potassium may be released from the fuel in numerous ways. Potassium is probably volatilized with organic species, and may be released as metallic K, although the latter is subject to rapid chemical reaction and its life time short. If the fuel contains chlorine, potassium probably appears as the salt, KCl. Without chlorine, the hydroxide, KOH, or alternatively potassium oxides, sulfates, or carbonates may be formed. Nearly all the inherent potassium in biomass is either water soluble or ion exchangeable (Baxter, et al., 1993), and readily volatilized, although not all does volatilize and much remains in the flyash and boiler bottom ash. Calcium, contained primarily in cell walls, is more refractory and less readily volatilized, although some may be released by similar mechanisms and in similar forms. Calcium may also enter through the introduction of limestone to the furnace. Under attack from chlorine, vaporized as HCl if the fuel contains it, volatilized potassium possibly forms KCl in the gas phase. Chlorine is probably an important facilitator in the deposition of alkali species on heat transfer surfaces. Starting with a clean surface, KCl, or KOH if chlorine is absent, is deposited on the surface through heterogeneous condensation or small particle transport following homogeneous condensation and nucleation, either in the bulk gas if sufficiently cooled, or in the thermal boundary layer adjacent to heat transfer surfaces. Thermophoretic mechanisms, in addition to condensation, are important to the deposit formation at this point due to the large thermal gradients above the surface (Raask, 1985;

Baxter, 1993). Past the flame, if the gas is sufficiently cooled, KCl or KOH may react with SO_2 or SO_3 in the gas to form potassium sulfate, K_2SO_4, which can condense and deposit (Raask, 1985; Hupa and Backman, 1983). Sulfation of the alkali and alkaline earth species also occurs once they are deposited on the surface by reaction with gaseous sulfur oxides, losing chlorine from the deposit in the process. There is some question as to which sulfation route is dominant, but the condensed phase process appears more likely. In this manner the surface initially acquires a characteristic thin, dense, and reflective deposit layer nearly universally observed. Following the initial deposit formation, particle impaction becomes the dominant mechanism for incorporating inorganic elements into the deposit. Condensation, phoretic forces, and chemical reaction still contribute to the deposit formation while suitable conditions exist.

Deposition of flyash, containing silicates and other species, and limestone or other additives, deposit by impaction if within a suitable size range. Particles smaller than about 5 µm tend to follow the streamlines around the tubes, while for larger particles rebounding from the surface is enhanced because of the high kinetic energy of the particles. Large particles have been observed rebounding from the upper tube surface in the MFC even after formation of a deposit. The particle size for which rebound becomes important has not been investigated for biomass. For tubes in cross flow, the deposit develops as a characteristic aerodynamic wedge on the upstream or leading edge of the tube, as in Figure 4 (p. 8). Heat transfer through the deposit is reduced as it thickens, and the deposit surface temperature increases toward the gas temperature. Condensation is no longer important where the deposit surface temperature exceeds the dew point, and thermophoresis becomes less important as the temperature gradient across the thermal boundary layer declines. Heterogeneous and homogeneous reactions cause continuing sulfation and the formation of complex silicates within the deposit. The less stable carbonates deposit in the cooler regions, downstream in the convection pass and in the wake regions of the tubes, as in the case of the bubbling fluidized bed unit, FBC-1. Continuing sulfation leads to increased deposit tenacity, making soot blowing less effective in removing deposits. Formation and deposition of alkali sulfates and chlorides also contributes to tube metal corrosion. This conceptual model is grossly simplified, but aids in the interpretation of the results obtained in both the full-scale and laboratory experiments. Features of the deposits from the different facilities appear consistent with these mechanisms.

None of the California units currently burns straw. The fouling rates with straw, even in low concentrations, have proven too high for economic operation. In contrast, the two Danish grate units described here are fueled entirely with straw, and operate several thousand hours each year, although deposition remains a concern. Despite the problems associated with slagging and fouling from straw fuels, Denmark has established a major program in straw combustion for district heating, electric power, and combined heat and power (CHP) generation. Currently about 70 plants, mostly small heating facilities, but including larger scale power units, burn straw from wheat, rye, and rape, alone or in combination with coal or wood. Although fuel costs are high, as much as $70 t^{-1} (Nikolaisen, 1992), and the cost of electric power from these plants around $0.10 kWh^{-1}, the sale of thermal energy improves the economic performance, and Danish CO_2 laws provide subsidies to "alleviate any negative consequences caused by the conversion to biomass fuels." Many of the plants utilize the folded furnace design shown in Figure 1 (p.6), providing greater surface area, and reducing gas temperatures ahead of

the critical crossflow superheater surfaces to below 750° C (1400° F) or lower, which mitigates the problem of superheater fouling. The design utilizes parallel heat exchangers in the folded section following the radiant furnace to reduce the deposition by impaction. All of the California facilities investigated for this study normally operate with furnace exit gas temperatures in the range of 850° to 950° C (1600° to 1750° F) to achieve peak capacity. Reducing furnace exit gas temperature might help to reduce the severity of superheater and convection pass fouling in the California facilities, but the impact on capacity and economy of the plants is not yet known. In this sense, the boilers erected to burn agricultural fuels in California appear to have been underdesigned. The concepts employed in the Danish boilers are not unique, and were adapted from boilers burning solid waste and other high fouling fuels.

The reduction of furnace exit gas temperature to reduce the severity of superheater fouling follows from the mechanisms of deposit formation discussed above, although operators know empirically that fouling is generally reduced by lowering the exit gas temperature. If the alkali and other fouling compounds are homogeneously condensed, or heterogeneously condensed on flyash, prior to crossing the superheaters, particle transport along the streamlines of the flow reduces the amount of substance depositing. For particles diffusing to or impacting the surface, rapid cooling and solidification while crossing the thermal boundary layer reduces the number of particles adhering to the surface. If the exit temperature is low enough, the particles will solidify in the bulk gas. Reduced temperatures also result in reduced chemical reaction rates. The strength of the deposit formed is reduced, which makes it easier to remove by soot blowing. Disadvantages of the method are associated with the costs of building larger furnaces to accommodate the reduced heat transfer coefficients on the parallel heat exchangers, loss of efficiency if high superheat temperatures cannot be attained, and possible derating of capacity and loss of revenue for existing units. Deposit-related corrosion may also be enhanced at lower temperatures. As a short term remedial problem for existing units, the technique may be effective, employed either continuously or on an intermittent basis. Intermittent operation at lower temperature may contribute to weakening of deposit through thermal cycling, also making soot blowing more effective.

Of some interest is the recent Danish experience with so-called "gray" straw, or straw that has been exposed to rain in the field. In the last year, much of the straw was washed by natural precipitation, and problems with boiler fouling were reduced. Plant capacity was also reduced due to higher moisture and reduced organic matter content of the fuel. However, as with bagasse, leaching of the straw appears to offer a substantial benefit in the control of fouling deposits in the boilers, and emphasizes the role of potassium and chlorine, which are both readily leached. In California, rain leached, spring harvested, rice straw might be acceptable for existing boilers, but probably only when blended at a low concentration with more conventional fuels. Artificial straw washing has not been investigated and the feasibility of such a technique is unknown.

Additives may hold some promise for reducing the rate of fouling. Fluidized bed combustion power plants, as in the units described here, routinely employ limestone injection for control of sulfur emissions, with additional benefits in reduced bed agglomeration. Limestone addition is involved in the formation of calcium sulfate deposits on superheaters and other convection pass surfaces. Other additives, such as kaolin, dolomite, or magnesium oxide, have been used to reduce bed agglomeration and

slagging, but they have so far not been widely employed in the industry, and are generally particularly effective only with fluidized beds because of the good mixing. The effect of additives is frequently debated, but so far no systematic study of their potential for biomass combustors has been undertaken. Standardized methods to test the effect of additives on biomass fuel ash behavior are not developed, and standard ash fusibility tests to determine deformation and fusion temperatures of ash are now commonly accepted as being of little value in predicting the behavior of ash in biomass boilers. Such tests generally fail because they do not properly simulate elemental composition and enrichment in deposits, nor the physical conditions leading to deposit formation.

For the existing facilities, retrofit designs can be conceived to increase the number of acceptable fuels; but without major capital investment, strategies are limited principally to changing boiler operating conditions in concert with changes in fuel properties (e.g., furnace exit gas temperature control with fuel selection). Design changes might include the addition of a thermal gasifier on-site to essentially pretreat the fuel ahead of the boiler. Gasifying high fouling fuels and only burning the gas in the boiler might alleviate or reduce ash fouling. The purpose would be to retain inorganic materials, including alkali, in the char phase, which would be disposed of in some other fashion. If sufficiently depleted in carbon, the char could be land applied for its fertilizer value, although there are significant unresolved questions concerning the feasibility and suitability of the technology. The success of such measures depends on gasifying the fuel at lower temperatures than combustion; otherwise, under reducing conditions, the vaporization of fouling elements can be enhanced, exacerbating the problem of deposition. Other pretreatment options include fermenting the fuel and burning the residual solids, which should be leached of potassium and chlorine. At least one facility has already been proposed in California employing a fermentation option for rice straw, although not specifically as a pretreatment for combustion. The feasibility of the technology has not yet been demonstrated in a full-scale unit.

Many of the problems encountered with ash fouling in existing units accrue from the lack of prior experience in the industry in burning a wide variety of fuels. Improved and advanced combustor designs and concepts are available, although many have not been adequately tested. Other concepts, such as integrated gasifier combined cycles and numerous variations, are under active development and include research into the control of alkali species. Substantial improvements should be possible as existing units are retired and replaced, although fouling problems are not likely to become fully mitigated. Economic analyses should include careful accounting of operating costs in addition to capital costs for the facilities.

Conclusions

Many agricultural fuels have proved unsuitable for use in existing biomass boilers. Straw and other annual herbaceous plant materials cause rapid fouling of heat transfer surfaces, furnace slagging, and agglomeration of fluidized beds. Excessive deposition results from the incompatibility of fuel composition with boiler design and operation. Superheater fouling is perhaps the most critical problem for existing units. Clearly, deposit formation occurs as a result of complex interactions among many compounds, and cannot be described on the basis of potassium, silicon, or any other element alone.

Full-scale experiments and laboratory simulations show the composition of deposits to be consistent with postulated mechanisms of deposit formation and growth, although details of the routes by which elements are incorporated into the deposit remain to be elucidated. In biomass, unlike coal, and with a few exceptions, the major alkali is potassium rather than sodium. In herbaceous species, including straws and grasses, canes and stovers, inherent potassium concentrations are about 1% of the fuel dry weight, almost all of which is available for volatilization during combustion. These same fuels are frequently rich in chlorine, silicon, and sulfur, which in combination with potassium represent the primary fouling agents when these fuels are burned. Chlorine is an important facilitator, leading to the condensation of potassium chloride salt on surfaces, which is readily attacked by sulfur oxides to form potassium sulfate, and leads to the creation of sticky coatings for enhanced particle attachment following inertial impaction. Potassium, sometimes in combination with alkaline earth metals like calcium, reacts with silicates deposited as fly ash to form molten glassy phases leading to tightly sintered structures. In the furnace, glass reactions lead to the formation of heavy slag deposits resembling fuel ash in composition but substantially depleted in sulfur. On superheater surfaces in boilers firing wheat straw, chlorides represented a major portion of the deposit mass.

When firing wood fuels, either in combination with agricultural fuels such as hulls, shells, and pits, or woods derived from urban sources with potentially large amounts of adventitious material contamination, the role of potassium may be reduced and that of the alkaline earth metals such as calcium more pronounced. Fuels comprised principally of mature stem wood have relatively low inherent potassium concentrations, around 0.1% and low inherent silicon and chlorine concentrations. Initial deposition, possibly as condensation of hydroxides, is followed by sulfation of alkali and alkaline earth elements, increasing the tenacity of the deposits. If large amounts of adventitious materials in the form of clays or other soil contaminants are present, the role of silicon may still be quite pronounced in secondary deposit growth by particle impaction following the initial formation of condensed layers on surfaces. Complex alkali-alkaline earth-aluminosilicates form or are incorporated into superheater deposits in this manner. Although mature wood is low in silicon, urban and agricultural wood fuels used commercially all had substantial silicon concentrations in the ash. Injection of limestone into fluidized bed combustors leads to the formation of calcium sulfate deposits on superheaters where sulfur is present in the fuel. Wood fuels and blends fired commercially, although generally low in sulfur, had adequate amounts to cause substantial sulfation of deposits. Calcium sulfate was especially pronounced in the superheater deposits in fluidized beds, compared with the grate units.

Laboratory simulations confirmed the enrichment of alkali species in the early phases of deposit formation. For straws and grasses, initial deposits containing alkali chlorides can be expected. A wood blend with small amounts of almond shell produced a sulfated deposit similar to that observed in commercial units burning similar fuels. Potassium rich almond hulls and shells generated deposits containing more potassium than could be accounted for as sulfates and chlorides. Sodium rich olive pits produced a similar result. With such fuels, initial deposition as alkali hydroxides or carbonates may be important.

5. BOILERS, FUELS AND DEPOSIT FORMATION

The alkali deposit investigation combined field experience with laboratory investigations of a variety of biomass fuels. Biomass power plants typically fire blends of biomass fuel. Fuel choices are often based on reliability of supply, cost and availability. As described previously this investigation included deposits from blends of wood, urban wood and agricutural residues and within that included deposits from highly alkaline fuels such as straw and manures. Deposit mechanisms were investigated including condensation and chemical reaction, particle impaction and thermophoresis and combinations of mechanisms. Finally, the project attempted to evaluate potential fouling and slagging indicators such as an index of alkali concentration, and thermal ashing methods. This section summarizes the general conclusions from those investigations.

Deposits from Blends of Wood and Agricultural Residues

Four of the plants fired wood or urban wood waste blended with agricultural residues including prunings, pits, nuts, shells and straw. Tables 4, 5, 7, 8 and 9 illustrate the composition of ash from the fuel and the deposits. The fuel burned in the bubbling fluidized bed boiler, FBC-1, for example, was a mixture of wood and agricultural prunings. It was relatively low in ash; however, it contained sufficient alkali to produce troublesome deposits in the convection passes of the boiler even with the addition of limestone. Deposits accumulated on feed tubes and other hot protuberances. Furnace wall deposits are similar in composition to the ash of the unburned fuel, except for the depletion of chlorine, sulfur, phosphorous and part of the alkali. Deposits on superheater tubes perpendicular to the flow, as shown in Figure 37, were solid but granular in texture. Alkali sulfates and calcium carbonates were found in the wedge-shaped deposits of the screen tubes and the superheaters. Potassium chlorides were found on superheater tubes. Corrosion was also evident in the convection passes. As discussed in Section 4 the pattern of deposits was similar for fluidized beds, circulating fluidized beds and spreader stokers with similar fuel compositions and furnace exit gas temperatures. Severe deposition occurred with higher temperatures and increasing concentrations of the volatile inorganic elements in the fuel.

Deposits from Highly Alkaline Fuels

Deposits from highly alkaline fuels were observed with straw fired on the traveling grates, illustrated in Figure 1, and in the suspension fired Multi-Fuel Combustor (Figure 28). A traveling grate boiler in California, Grate-1, has a spreader stoker that was designed primarily for wood. The Sandia Multi-Fuel Combustor burns finely divided fuel while entrained in a hot gas flow. The Danish stokers, Grate-2, Grate-3, push straw gently onto a cooled grate. Reports and analyses were also received from a similar boiler firing chicken manure with wood.

Tables 5 and 7 show the analyses of fuels and deposits in the spreader stoker traveling grate boiler (Grate-1) when firing a blended fuel composed of 80% urban wood and 20% straw. Like the bubbling fluidized bed, deposits on the grate and fireside refractory are similar in composition to the fuel except for the volatile alkali and sulfur. Those deposits on or near the grate, or near high temperature flames, were either glassy fused coatings or agglomerates of ash bonded together with a glassy material as shown

in Figures 7 and 34. The cool upper waterwall, above the flyash impingement zone, showed a white condensation layer of potassium sulfate and some chlorine. Deposits on superheater tubes perpendicular to flow were mostly granular, extending in wedge shapes from the upstream surface into the gas stream. Particulates were often encased with alkali silicates as shown in Figure 33. The superheater deposits showed the enrichment of alkali sulfate, chloride and calcium carbonates. Erosion studies in a commercial laboratory showed that hard silica and alumina combined with the chemically active chlorine, potassium and sodium to make the flyash from this boiler more erosive than others. Further studies are needed for similar fuels in other boilers. Gasification was considered as one means to reduce alkali and flyash carryover in the boiler, where the dirty wood fines and straw would be gasified at low temperature with additives and the cleaner product gas would be fired in the boiler.

Potassium compounds were typical bonding agents between silica or media particles in superheater deposits. In some cases the potassium reacted with the silica to form a bonding glass. This was shown in the SEM photo (Figure 39) of three particles of fluidized bed sand (CFB-1) cemented together with a glass containing 6% K_2O after burning a blend of 15% almond hulls with urban wood waste and in the agglomerated bottom ash from firing a blend of wood with 20% wheat straw in Grate-1. For example, a circulating fluidized bed boiler in Denmark required special ash chemistry and additives, including temperature control to fire wheat straw with coal.

Table 7 compared the fuel ash and deposits in Danish straw fired boilers of the folded furnace design (Grate-2, Grate-3). These boilers are designed for high ash fuels. They have high waterwall surface areas, ample volume, low gas velocities, and low furnace exit gas temperatures. Like the fluidized bed and wood stoker, the deposits at the grate are similar in composition to the fuel, with depletion of some of the volatile species. Furnace wall and convection sections were heavily coated with potassium chloride that inhibited heat transfer. Enrichment of potassium sulfate and potassium chloride is evident in the superheater deposits. Alkali, chlorine and sulfur are also evident in the dust collector flyash where severe corrosion occurs.

A separate superheater fired with producer gas from straw may be fitted to one of these boilers (Grate-3) allowing the boiler to operate at low furnace exit gas temperatures thereby reducing deposits in the superheaters. Low alkali, low acid gas from low temperature (600° C) pyrolysis would be burned to superheat steam from the straw boiler to higher pressures for power generation. Char would be taken to a landfill.

Highly alkaline fuels, straw, pits, nuts, shells and manures, provide low melting alkaline compounds that react with sulfur and chlorine to form deposits or agglomerate silica particles for ash or fluidized bed media. Even when burned alone these fuels require low temperature furnace conditions and frequent flyash or deposit removal. This project demonstrated that even with specially designed furnaces the highly alkaline fuels present serious operational problems to boiler operators that cannot be avoided by simply blending fuels.

Deposit Mechanisms

Deposits observed in this project are consistent with all known mechanisms for deposit formation: particle impaction, condensation, thermophoresis and chemical reaction (Baxter, 1993). These transformations are depicted by Bryers (1994) in Figure 40, based on observations from the project. Deposition mechanisms can be divided into those dealing with gases, such as condensation and chemical reaction, and those dealing with particles such as particle impaction.

Condensation and Chemical Reaction

Alkali, sulfur and chlorine vaporize during combustion and condense as sulfates or chlorides on flyash, or deposit on waterwalls. Surfaces oriented parallel to the gas flow and subject to deposition by condensation and diffusion of small particles, but free of impaction by large particles, will collect a thin film of potassium sulfate or other compounds, e.g. $CaSO_4$. This was observed in the spreader stokers firing wood with straw, wood with chicken manure, and straw alone. This deposition is unavoidable. The original boiler design must allow for the loss in adsorption due to this fouling; otherwise the boiler must be derated or the power plant must add heating surface.

Operating a furnace at partial load on wood and straw demonstrated the formation of sulfur compounds by condensation. Furnace gas exit temperatures were 760° C (1400° F). Reflective white ash deposits appeared in the upper furnace and in convective passes. High sulfur concentrations, as in the upper furnace wall deposits, indicated that alkalis occurred as sulfates. The absence of silicon, aluminum, iron, titanium, or other refractory compounds indicated that few particles accumulated in the region. It is likely that potassium originated from the straw and formed a vapor during combustion. Since this region of the furnace has low particle impact, deposits form primarily through condensation and chemical reaction. There is a question as to whether this is heterogeneous condensation or homogeneous condensation. It could also be condensation on particles and then particle deposition on the walls. Similar deposits occurred when manure was fired in combination with wood in a folded furnace designed boiler, similar to that shown in Figure 1 (Grate-3).

Particle Impaction and Thermophoresis

Flyash impacts on the walls and is the major contributor to the total biomass deposit on the walls, as shown in Table 7 and Figure 7, except in stagnation zones outside the main gas flow and cross flow superheater tubes. Since a liquid phase on the flyash surface will make it sticky, deposition will be primarily by inertial impaction of large particles and chemical or thermophoretic diffusion of the small particles. The energy of particles is important as well. Large particles with high kinetic energy may rebound from the surface after impaction. Very small particles are more likely to follow the streamlines and miss the surface. Deposition occurs primarily on surfaces immersed in the gas stream perpendicular to flow such as screen and superheater tubes, and those positioned farthest upstream. Below 730° C to 760° C (1350° F to 1400° F) fouling is apparently minimal and can be controlled by sootblowing. These temperatures are a few degrees below the melting temperature of certain eutectic mixtures formed by the condensation of potassium compounds. The furnace exit gas temperature in most biomass boilers is 850° C to 955° C (1560° F to 1750° F) which would suggest that

surfaces are probably sticky. Experience with sootblowing in the test plants has varied. The effectiveness of sootblowing depends on deposit tenacity which can only be predicted empirically. Most plants are still looking for more effective combinations of sootblowing and additives to minimize deposits or reduce deposit tenacity.

Combinations of Mechanisms

Deposits on slag screens at the entrance to the convection passes exhibit a combination of alkali condensation followed by sulfation and particle impaction as shown in Tables 8 and 9. The composition of these deposits is intermediate between the particle-dominated wall deposits and the condensate-dominated wall and ceiling deposits in stagnation zones.

Fouling and Slagging Indicators

Sticky temperatures of the ash or flyash, concentrations of alkali in the fuel, and tendency to form sulfates are a few indicators of potential slagging or fouling problems. Various methods were tested to determine stickiness in biofuels without success. For example, the stickiness of flyash in a sulfur or chlorine-free fuel can be predicted by differential thermal analysis (DTA) or similar techniques in the laboratory, in which case only the endotherms above 950° C -1000° C may apply (Bryers, 1994). But sulfur is present in most biomass fuels being fired, and the melting temperatures cannot be predicted by laboratory characterization since they are dependent upon post-combustion reactions and physical state changes. In this case one must know how the elements occur in the fuel and how they react in the boiler.

One method the coal industry developed to classify various coals relative to slagging and deposits involves calculating the weight in alkali oxides (K_2O + Na_2O) per heat unit, kg/GJ (lb./million Btu) in the fuel using the higher heating value (HHV). The calculation is:

$$\frac{1x10^6}{HHV \ kJ \ / \ kg(dry)} \ x \ Ash\%xAlkali\% \ in \ Ash = \frac{kg \ Alkali}{gJ}$$

or:

$$\frac{1x10^6}{HHV \ Btu \ / \ lb(dry)} \ x \ Ash\%xAlkali\% \ in \ Ash = \frac{lb \ Alkali}{MMBtu}$$

This method combines all of the pertinent data in one index number. Plant experience and field tests have shown that a slagging risk increases above 0.17 kg/GJ to 0.34 kg/GJ (0.4 lb. to 0.8 lb./MMBtu). Above 0.34 kg/GJ (0.8 lb./MMBtu) the fuel is virtually certain to slag and foul to an unmanageable degree. Alkali concentrations for many biofuels are shown in Figure 41 and in Appendix C. While an indicator of potential problems this information must be combined with field experience and boiler operating conditions to evaluate the impact of a fuel on a particular boiler.

An index for fouling tendency that is also based on alkali and alkaline earths was developed by Hupa and Backman (1983) where boilers are cofired with bark, coal and oil. The proportion of sulfate forming compounds (water soluble $CaO + MgO + Na_2O + K_2O$) is expressed as a percent of total ash in the fuel that goes to the boiler. In this investigation we found that water soluble sulfate-forming compounds made up 6% of the ash in a wood-almond fuel and 25% of the ash in wheat straw, of which 86% to 90% were alkali oxides. While the water soluble fraction made up 45% of the total alkali in the wood-almond fuel blend, more than 90% of the alkali oxides in wheat and rice straw were water soluble. It would appear that water soluble alkali could be a reasonable measure of fouling tendency where sulfur is present. Chlorine content must also be considered since some straws contain more chlorine than sulfur.

However, the slagging tendency of a boiler cannot be anticipated in terms of fuel properties alone. While the tendency to slag generally increases with increasing alkali content, the form of the alkali and other inorganic constituents as well as boiler operating conditions and boiler design have large impacts on deposit properties. This project delineated the major variables causing slagging. A conceptual description of deposit generation was proposed and both field and laboratory data were gathered to test it. The description remains to be formalized in the form of a computer program that incorporates fuel properties, boiler operation, and boiler design in predictions of ash deposition and deposit properties throughout the boiler.

Figure 41 Wood Fuels With High Annual Growth Are Abundant in Alkali, Sulfur and Chlorine
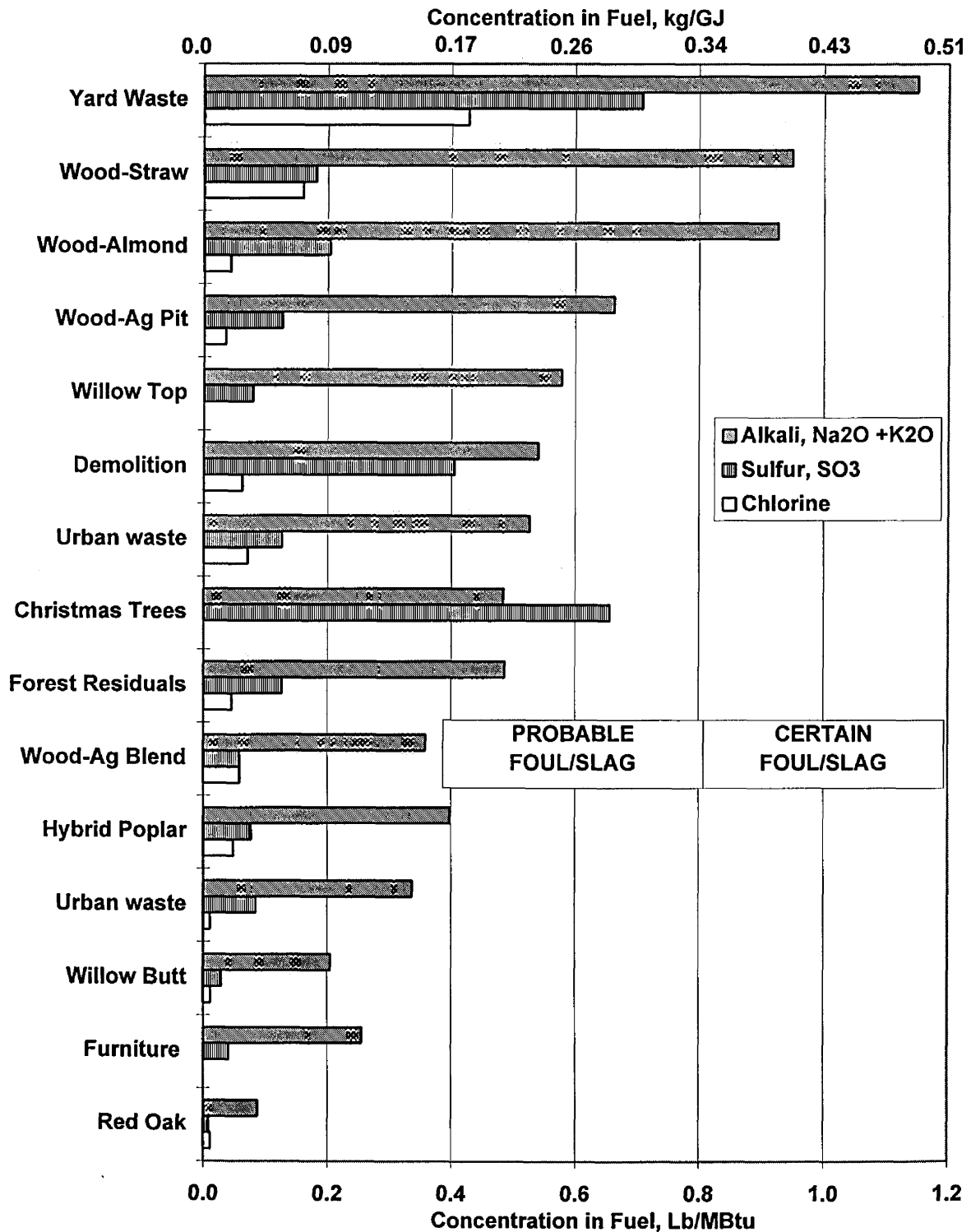
6. CONCLUSIONS

The investigation has led to a closer understanding of the very complex chemistry and formation of deposits. Conventional boilers do not provide the special conditions required to burn high percentages of agricultural residues or alkali laden fuels. New boiler designs are necessary to control combustion and furnace exit temperatures and to remove alkali and alkali compounds as they form on boiler grates, in the bed, on walls or on convective surfaces. Fluidized beds can fire somewhat higher percentages of alkali fuels due to the intimate mixing of inhibitors or additives with the burning fuel, but deposits still form from volatile elements. Gasification or pyrolysis may be used to reduce alkali volatilization from biofuels but retrofits to existing boilers need to be demonstrated in industry.

The investigation has generated a useful database of elemental analyses of biofuels and their ash that significantly expands the information that was available before the study. Sponsoring companies have learned more about what fuel and deposit analyses to request and how to interpret the results. Additional biofuel ash characterization studies are needed.

A variety of methods are used for proximate, ultimate and elemental analyses. For most purposes routine analyses of biomass for fuel should include proximate and ultimate analyses with microwave or low temperature (600° C) thermal ashing prior to analysis of ash elements, chlorine, fuel particle size and water soluble alkali.

One very positive result has been an increased awareness on the part of the participating plants of the importance of fuel quality, of establishing and enforcing specifications, of proper yard management, and of controlling fuel blends. Future projects by industry, government and academia should investigate erosion, corrosion and the potential of gasification to reduce deposits from biomass fuels.

Industry participants identified erosion, corrosion and design of boiler systems to convert high alkali fuels as the principal research needs. They expressed the need to: develop algorithms which correlate fuels, boilers and boiler operation with deposition; further characterize fuels and deposits; and validate and test alkali project results.

The development of predictive algorithms that can be used by industry to evaluate the potential deposition and corrosion from biomass fuels will require further analysis of fuel and deposit characteristics. More data will make better correlations between significant fuel elements (K, Na, S, Cl, P, Si) and deposits possible. While deposits were identified here, physical properties of deposits such as reflectivity, emissivity, mass, volume and porosity were not measured. A reliable automated deformation or sticking temperature analysis for empirical assay should be developed.

This project demonstrated the usefulness of parallel testing at the pilot scale and industry scale. Pilot scale boilers should be used for deposition and corrosion design studies. Controlled studies should also evaluate deposition rates on tube surfaces at different tube temperatures. Controlled tests should evaluate the effect of additives for reducing deposition rates with biomass fuels. Coupled thermal-chemical boiler models can be used to elaborate deposition algorithms.

Field tests should evaluate the effects of reduced firing rates on boilers including effects on capacity, furnace exit gas temperatures, severity of deposition, and corrosion. Alternative sootblowing techniques or other removal systems and tube spacing effects should also be tested. Gasification tests of high alkali fuels where the producer gas is fired in a boiler would demonstrate char reduction, effects on deposition and corrosion rates. An evaluation could be made of a biomass boiler with natural gas fired superheaters decoupled from the biomass combustor to avoid tube deposition. Tests should determine costs, qualifying status and natural gas demand as a portion of plant fuel use.

ACKNOWLEDGMENTS

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APPENDIX

A. Project Participants

B. Methods of Sampling and Analysis

C. Fuel Characteristics: Data Summary

D. Deposits

APPENDIX A. PROJECT PARTICIPANTS

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Hampton, New Hampshire and Anderson, California

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Randy Bates, Tim Smith
Woodland Biomass Power, Ltd., Woodland, California

Alkali Deposits

Found in Biomass Power Plants
A Preliminary Investigation of Their Extent and Nature

ANALYTICAL REQUEST FORM
(One Form Per Sample)

Plant:_____

Date:_____

AD4-3 February 1993
NREL Subcontract TZ-2-11226-1

USDOE/NREL - T. R. Miles - U.C. Davis - Bureau Mines - Sandia - Biomass Power Producers

Form Submitted By: _____

Sample taken at (location): _____

Sample Identification:_____

_____

Fuel Analysis:

____ **UPB + Chlorine (Ultimate, Proximate, BTU combined + Cl** ASTM D4208)

    ____ Ultimate (Moist, C, H, N, S, O, Ash)

    ____ Proximate (Moist., Ash, Volatile, Fixed C)

    ____ BTU (Calorific Value)

____ **Chemical Fractionation Test (incl. Ash analysis, Total Ash, Cl)**

Ash Analyses:

____ **Elemental Ash Analysis (Si, Al, Ti, Fe,Ca, Mg, Na, K, P, S, Cl)**

Deposit Analyses:

____ **Elemental Ash Analysis (Si, Al, Ti, Fe,Ca, Mg, Na, K, P, S, Cl)**

Other:

    _____ Sample Preparation_____

    _____ Chloride (if separate) - water soluble AOAC 969.10 (was 7.106), potentiometric____

    _____ Ash Fusion Temperature _____

    _____ Water Soluble Alkali_____

    _____ _____

    _____ _____

Samples shipped to:
Hazen Research, Inc.
4601 Indiana St.
Golden, CO 80403
Attn: Jerry Cunningham
Tel (303) 279-4501
Fax (303) 278-1528

Results and billing to:
Alkali Deposit Investigation
c/o Thomas R. Miles
Consulting Design Engineer
5475 S.W. Arrowwood Lane
Portland, OR 97225-1323
Tel (503) 292-0107
Fax (503) 292-2919

An Industry-USDOE Effort To Improve the Conversion of Agricultural and Urban Residues to Energy.

Appendix B.2 Standards for Biomass and Coal

ASTM - American Society of Testing and Materials (ASTM), Philadelphia, PA,
AOAC - Association of Official Analytical Chemists (AOAC), Washington DC.
Preferred methods are <u>underlined</u>.

<u>Standard -Title</u>

D. 1857	Fusibility of coal and coke ash
<u>D. 2015</u>	Gross calorific value of coal and coke by the adiabatic bomb calorimeter
D. 2361	Chlorine in coal
D. 2492	Forms of sulfur in coal
<u>D. 2795</u>	Analysis of coal and coke ash
D. 3172	Proximate analysis of coal and coke
D. 3173	Moisture in the analysis sample of coal and coke
D. 3174	Ash in the analysis sample of coal and coke from coal
D. 3175	Volatile matter in the analysis sample of coal and coke
D. 3176	Ultimate analysis of coal and coke
D. 3177	Total sulfur in the analysis sample of coal and coke
D. 3178	Carbon and hydrogen in the analysis sample of coal and coke
D. 3179	Nitrogen in the analysis sample of coal and coke
D. 3286	Gross calorific value of coal and coke by the isoperibol bomb calorimeter
<u>D. 3682</u>	Major and minor elements in coal and coke ash by atomic absorption
<u>E. 870</u>	Analysis of wood fuels
<u>D. 1102</u>	Ash in wood
E. 105	Probability sampling of materials
E. 141	Acceptance of evidence based on the results of probability sampling
E. 691	Conducting an interlaboratory study to determine the precision of a test method
<u>E. 830</u>	Ash in the analysis sample of refuse-derived fuel
<u>E. 711</u>	Gross calorific value of refuse-derived fuel by the bomb calorimeter
<u>E. 775</u>	Total sulfur in the analysis sample of refuse-derived fuel
<u>E. 776</u>	Forms of chlorine in refuse-derived fuel
<u>E. 777</u>	Carbon and hydrogen in the analysis sample of refuse-derived fuel
<u>E. 778</u>	Nitrogen in the analysis sample of refuse derived fuel
E. 828	Designating the size of RDF-3 from its sieve analysis
<u>E. 871</u>	Moisture analysis of particulate wood fuels
<u>E. 872</u>	Volatile matter in the analysis of particulate wood fuels
<u>E. 873</u>	Bulk density of densified particulate biomass fuels
E. 885	Analyses of metals in refuse-derived fuel by atomic absorption spectroscopy
E. 886	Dissolution of refuse-derived fuel (RDF) ash samples for analyses of metals
E. 887	Silica in refuse-derived fuel (RDF) ash
<u>E. 897</u>	Volatile matter in the analysis sample of refuse-derived fuel
E. 926	Preparing refuse-derived fuel (RDF) samples for analyses of metals
E. 953	Fusibility of refuse-derived fuel (RDF) ash
E. 959	Characterizing the performance of refuse size-reduction equipment
E.1117	Design of fuel-alcohol manufacturing facilities
E.1126	Standard terminology relating to biomass fuels
E.1288	Durability of biomass pellets
D. 5115	Collecting gross samples and determining the fuel quality of RDF
D. 4442	Direct moisture content measurement of wood and wood-base materials
D. 4278	Wet ashing procedure for preparing wood samples for inorganic chemical analysis
D.1756-04	Carbon Dioxide in Coal
AOAC 14.7	Total metals sample preparation using microwave digestion
P 4.20	Quantitative analysis: P. S. K. Ca, Mg, Na, B. Zn, Mn, Fe, and Cu in botanical materials
Unnumbered	Chemical Fractionation Procedure, Sandia National Laboratories, Livermore, CA
Unnumbered	Water Soluble Alkali, Hazen Research, Golden, CO
Unnumbered	BuMines West Ashing Method, Bureau of Mines, Albany, OR

Source: B. M. Jenkins, Biological and Agricultural Engineering, University of California, Davis, CA

Appendix B.3 Summary of Analytical Methods Used

Several methods were used to analyze fuels and deposits in this project. Methods, testing laboratories and reports or references are indicated below.

Fuel Chemical Analysis includes:
Ultimate, Proximate, and Btu (heating value) Elemental analysis of ashed fuel, including: Si, Al, Fe, Ti, Ca, Mg, Na, K, S, P, Chlorine, and Ash fusion temperatures. See Table 3 and Appendix B.2. Labs: Hazen, Consol, Foster Wheeler, BuMines.

Thermal ash preparation following ASTM D 1102 (Test Method for Ash in Wood) at 600 °C (1112 °F) to reduce alkali loss. Labs: Hazen, Consol, Foster Wheeler.

Wet ashing by BuMines and UC Davis involves chemical digestion and direct measurement; sample is kept sealed when microwaved and volatile elements are not lost on heating. See Appendix B.4.

Chemical Fractionation measures the quantities of water-soluble, ammonium acetate-soluble, and hydrochloric acid-soluble salts through successive leachings. This method separates the various chemical states of the alkali metals in particular, and is conceivably an indicator of deposit activity in biofuels, as it is in coal. Labs: Hazen, Consol,BuMines

These procedures include soaking the fuel in water heated to 95° C (203 °F) for up to 16 hours and filtration followed by atomic absorption or emission spectrographic analysis. These methods can yield 5% to 15% more alkali than methods where ash is prepared at 600 °C or more. Results instructive but very difficult to extract leachate from wet biomass sample. See Appendix B.5, and Baxter (1994-1995).

Water Soluble Alkali and Low Temperature Ashing techniques use leaching and oxygen plasma ashing to measure alkali dispersed in plants as ions, hydroxides, carbonates or chlorides that can otherwise be lost in ash preparation. Labs: Hazen, Foster Wheeler, BuMines. (Bryers, 1994)

Water soluble portion is a low cost method to screen high alkali fuels. Low temperature plasma was used to make ash from the fuels for analysis. Found not to be representative because oxygen used in process makes chlorates and nitrates not normally found in biomass combustion. (Bryers, 1994)

X Ray Diffraction techniques determine the mineral and phase composition of fuel ash or deposits. Labs: Foster Wheeler, BuMines

Helped to distinguish between amorphous silicate (opaline) deposits characteristic of straw or leafy matter and crystalline deposits from wood, sand or dirt. (Oden 1993, 1994)

Differential thermal analysis (DTA)and thermogravimetric analysis (TGA) techniques measure material loss as ash or deposits are heated, to determine low-temperature melts (DTA), and low temperature losses caused by volatilization of the alkali (TGA). Labs: Foster Wheeler, BuMines.

Some melts are clear but it is difficult to interpret results for biomass ash. Method of ash preparation strongly influences results. Low temperature changes often due to decomposition or evaporation, not phase change or vaporization. (Bryers, 1993, 1994).

Sticky Temperature techniques determine the temperature that softens the surface of the alkali or ash, allowing it to stick to other surfaces and start the agglomeration process. Labs: Hazen

Intended for plant-scale fuel screening. Not adequate to simulate furnace conditions. (Miles, 1994).

Multi-Fuel Combustor is designed to accumulate deposits produced during combustion on a round pipe to simulate boiler tubes and waterwalls. Laser methods monitor rates of deposition. 11 fuels and blends analyzed. Composition of samples compared with those found in furnaces. Lab: Sandia. (Jenkins, et.al, 1994)

Scanning Electron Microscopy (SEM) examination of sections of ash and deposit samples to confirm mineral composition and observe mechanisms of deposit formation. Labs: BuMines, Sandia.

Observed fusion of amorphous silicates and alkali compounds, agglomeration mechanism of crystalline particles, confirmed composition determined by mineralogical and elemental analysis. (Oden 1993, 1994).

Molecular Beam Mass Spectrometry (MBMS) is being used at NREL to study in real time the sequence and concentrations of combustion products from the same biomass samples the project has analyzed by other methods, further complementing our understanding of the mechanisms of biomass combustion and provides direct observation of alkali vapor species. Lab: NREL.

Shows that salts and chlorides evolve rapidly on heating. Confirms the approach of following elements through the boiler to identify where and how they condense or concentrate in deposits. (French et. al, 1994, Dayton et.al, 1994)

Appendix B.5 Comparison of Microwave and Thermal Ashing

| Component | Bureau of Mines wet ashing method | | | | Thermal ashing method: H= Hazen | | | |
| | Rice Straw | Wheat Straw | Wood-Almond | Switch Grass | Rice Straw, H | | Wheat Straw, H | |
					ash	straw**	ash	straw**
SiO2	12.30	4.50	1.76	4.12	74.67	12.84	55.32	3.61
Al2O3	0.25	0.10	0.56	0.14	1.04	0.18	1.88	0.12
TiO2	0.09	0.01	0.04	0.01	0.09	0.02	0.08	0.01
Fe2O3	0.12	0.10	0.45	0.14	0.85	0.15	0.73	0.05
CaO	1.24	0.35	0.85	0.61	3.01	0.52	6.14	0.40
MgO	0.36	0.23	0.24	0.23	1.75	0.30	1.06	0.07
Na2O	0.12	0.19	0.22	0.08	0.96	0.17	1.71	0.11
K2O	2.68	1.97	0.37	0.51	12.30	2.11	25.60	1.67
S	0.12	0.22	0.03	0.03	0.50	0.17	1.76	0.14
P2O5	0.25	0.08	0.08	0.13	1.41	0.24	1.26	0.08
Cl	NA	0.22	0.76	0.03		0.54		0.21
Pct Ash	17.53	7.97	5.36	6.03	17.19		6.52	
Total O2 in ash	8.19	3.33	1.90	2.81				
Total metals in ash	9.34	4.64	3.46	3.22				
C	35.73	42.14	43.97	40.58		35.20		41.75
H	5.02	5.56	6.03	6.17		4.79		5.07
N	0.89	0.50	0.42	0.27		0.80		0.40
Nonmetal oxygen***	41.31	46.17	47.70	50.09		33.92		39.08
Total oxygen	49.50	49.50	49.60	52.90				
Undetermined	-0.48	-2.33	-3.48	-3.13		8.06		7.24
Total all components	100.00	100.00	100.00	100.00		100.00		100.00

All compositions wt pct. All materials in as-received condition.

** Calculated from pct ash and ash composition, except C, H, N, S, and O (by difference) from Ultimate analysis.

*** Total oxygen minus oxygen in ash.

Table 1. Biomass Analysis; Comparison Between Laboratories. Prepared 8-3-93. Updated 11-26-93. L. L. Oden, Albany Research Facility, US Bureau of Mines, Albany, OR.

Appendix B.6 Determination of Water-Soluble Alkali

Water soluble alkali is a simple and potentially useful method to monitor alkali contet in fuels and fuel blends. The following procedure is used by Hazen Research, Inc., Golden Colorado.

All lab ware that comes in contact with the sample must be scrupulously clean and free of sodium and potassium contamination. Wash the plastic volumetric flask with 1:1 HNO_3 just prior to use. Rinse with deionized water 3 times following the acid wash.

Carry a blank along with the samples to detect and quantify any contamination that may be present.

PROCEDURE

1. Weigh a 10.00 gram sample of 60 mesh *air-dry sample* into a 250 ml plastic volumetric flask. Use a funnel made from weighing paper to facilitate the transfer.

2. "Wet" the sample with 5 ml of ethyl (or methyl) alcohol. This will allow the fuel particles to absorb and be wetted readily by water added in the next step.

3. Add 100 ml of deionized water to the sample, and swirl the flask to assure that the sample has been thoroughly wet by the solution,

4, Place the flask in a hot water bath on a hotplate set so that the water bath is just at, or slightly under, boiling temperature. Allow the sample to digest at this temperature for 16 hours. The 16 hour digestion time can be accomplished in two 8 hour periods.

5. Remove the flask and allow the contents to cool. Dilute to volume with deionized water and mix well.

6. Allow the particulates to settle out, and decant a portion of clear solution into a plastic 15 dram vial.

7. Submit the vial to the AA laboratery for analysis for soluble sodium and potassium, reported as the oxides. The AA lab will dilute the solution 1:10 to put it into the correct matrix to match the AA calibration standards.

8. Submit, along with the sample, a completed Analysis Report data form.

9. Calculate the % water soluble sodium and potassium using the Apple II computer program entitled "AA". Report results to the nearest .001 %.

Gerald Cunningham, Analytical Department, Hazen Research, Inc. 4601 Indiana, St. Solden, CO 80403. (303) 278-1528.

Fuel	Fuel Blend CFB-1		Fuel Blend FBC-1		Fuel Blend Grate-1		Fuel Bend CFB-3		Fuel Blend CFB-2		Fuel Blend Grate-1	
Type	Urban wood - Ag		Urban wood - Ag		Urban wood		Wood-Pit		Wood-Almond		Wood-20% Straw	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis												
Fixed Carbon	12.36	19.79	13.02	16.93	12.69	15.23	11.55	18.10	12.32	15.94	15.45	16.67
Volatile Matter	47.40	75.89	62.02	80.57	66.02	79.23	48.95	76.77	59.77	77.28	69.65	75.14
Ash	2.70	4.32	1.93	2.50	4.62	5.54	3.27	5.13	5.25	6.78	7.59	8.19
Moisture	37.54	--	23.03	--	16.67	--	36.23	--	22.66	--	7.31	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis												
Carbon	32.13	51.44	38.24	49.69	40.64	48.77	31.00	48.62	36.7	47.45	44.01	47.48
Hydrogen	3.54	5.67	4.51	5.87	4.8	5.76	3.68	5.78	4.28	5.53	5.38	5.81
Oxygen	23.81	38.13	32.01	41.57	32.99	39.59	25.36	39.76	30.6	39.57	35.28	38.05
Nitrogen	0.26	0.41	0.25	0.33	0.22	0.27	0.42	0.65	0.45	0.59	0.32	0.35
Sulfur	0.02	0.03	0.03	0.04	0.06	0.07	0.04	0.06	0.06	0.08	0.11	0.12
Ash	2.7	4.32	1.93	2.5	4.62	5.54	3.27	5.13	5.25	6.78	7.59	8.19
Moisture	37.54	--	23.03	--	16.67	--	36.23	--	22.66	--	7.31	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	5,506	8,815	6,449	8,379	6,967	8,361	5,388	8,450	5,281	6,829	7,492	8,083
Chlorine %	<0.01	0.01	0.04	0.05	0.05	0.06	0.02	0.03	0.02	0.03	0.12	0.13
Water Soluble Alkalis %												
Na_2O	0.008	0.013	0.034	0.044								
K_2O	0.097	0.155	0.132	0.172								
CaO		0.226										
Elemental Composition												
SiO_2		39.96		28.81		55.12		52.55		45.60		55.50
Al_2O_3		12.03		8.47		12.49		13.15		10.75		9.37
TiO_2		0.87		0.83		0.72		0.43		0.54		0.50
Fe_2O_3		7.43		3.28		4.51		8.18		4.06		4.77
CaO		19.23		27.99		13.53		10.06		18.96		11.04
MgO		4.30		4.49		2.93		3.27		4.22		2.55
Na_2O		1.53		3.18		3.19		5.90		3.08		2.98
K_2O		5.36		8.86		4.78		5.04		6.26		6.40
SO_3		1.74		2.00		1.92		2.10		2.06		1.80
P_2O_5		1.50		2.57		0.88		1.90		1.47		1.04
CO_2		6.05		6.07								
Undetermined				3.45		-0.07		-2.58		3.00		4.05
TOTAL		100.00		100.00		100.07		100.00		100.00		100.00
Alkali, Lb/MMBtu		0.34		0.36		0.53		0.66		0.93		0.95

Fuel	Wood		Wood		Wood		Wood		Wood		Wood		Wood		Wood	
Type	Red Oak Sawdust		Fir Mill Waste		Furniture Waste		Hybrid Poplar		Alder/Fir Sawdust		Poplar-Coarse		Forest Residuals		Christmas Trees	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis																
Fixed Carbon	11.92	13.47	6.47	17.48	11.77	13.39	11.63	12.49	9.14	19.31	11.44	12.26	6.96	13.62	12.93	20.80
Volatile Matter	76.35	86.22	30.38	82.11	72.98	83.00	78.97	84.81	36.27	76.56	80.33	86.14	42.10	82.41	46.02	73.99
Ash	0.28	0.31	0.15	0.41	3.18	3.61	2.51	2.70	1.96	4.13	1.49	1.60	2.03	3.97	3.24	5.21
Moisture	11.45	--	63.00	--	12.07	--	6.89	--	52.63	--	6.74	--	48.91	--	37.81	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis																
Carbon	44.24	49.96	18.95	51.23	43.85	49.87	46.72	50.18	24.17	51.02	47.39	50.82	25.7	50.31	32.09	51.59
Hydrogen	5.24	5.92	2.21	5.98	5.2	5.91	5.64	6.06	2.75	5.8	5.49	5.89	2.35	4.59	3.47	5.58
Oxygen	38.76	43.77	15.66	42.29	35.42	40.29	37.66	40.44	18.25	38.54	38.32	41.08	20.42	39.99	22.82	36.70
Nitrogen	0.03	0.03	0.02	0.06	0.25	0.29	0.56	0.6	0.22	0.46	0.55	0.59	0.53	1.03	0.32	0.52
Sulfur	<0.01	0.01	0.01	0.03	0.03	0.03	0.02	0.02	0.02	0.05	0.02	0.02	0.06	0.11	0.25	0.40
Ash	0.28	0.31	0.15	0.41	3.18	3.61	2.51	2.7	1.96	4.13	1.49	1.6	2.03	3.97	3.24	5.21
Moisture	11.45	--	63.00	--	12.07	--	6.89	--	52.63	--	6.74	--	48.91	--	37.81	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	7,415	8,374	3,248	8,779	7,613	8,658	7,615	8,178	4,150	8,760	7,590	8,139	4,429	8,670	5,603	9,009
Chlorine %	<0.01	<0.01	0.07	0.19	<0.01	<0.01	0.01	0.01	<0.01	0.02	0.04	0.04	0.02	0.04		
Water Soluble Alkalis %																
Na_2O	<0.001	0.001	0.051	0.139					0.004	0.009						
K_2O	0.069	0.078	0.019	0.051					0.086	0.181						
CaO	0.017	0.019														
Elemental Composition																
SiO_2		20.97		15.17		57.62		5.90		35.36		0.88		17.78		38.89
Al_2O_3		2.99		3.96		12.23		0.84		11.54		0.31		3.55		14.74
TiO_2		0.27		0.27		0.50		0.30		0.92		0.16		0.50		0.36
Fe_2O_3		2.94		6.58		5.63		1.40		7.62		0.57		1.58		9.30
CaO		10.90		11.90		13.89		49.92		24.90		44.40		45.46		9.50
MgO		4.15		4.59		3.28		18.40		3.81		4.32		7.48		2.52
Na_2O		1.40		23.50		2.36		0.13		1.71		0.23		2.13		0.53
K_2O		22.40		7.00		3.77		9.64		5.75		20.08		8.52		7.86
SO_3		2.69		2.93		1.00		2.04		0.78		3.95		2.78		11.36
P_2O_5		1.33		2.87		0.50		1.34		1.90		0.15		7.44		2.40
CO_2/other		14.30		18.92				8.18		1.85		19.52				
Undetermined		15.66		2.31		-0.78		1.91		3.86		5.43		2.78		2.54
TOTAL		100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu		0.09		0.14		0.26		0.32		0.35		0.40		0.49		0.49

Fuel	Wood		Wood		Wood		Waste Paper		Refuse Derived Fuel		Currency	
Type	Demolition		Land Clearing		Yard Waste		Mixed Waste Paper		Tacoma		Shredded	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis												
Fixed Carbon	11.21	12.32	7.04	13.87	8.41	13.59	6.78	7.42	0.45	0.47	11.13	11.67
Volatile Matter	67.84	74.56	35.38	69.63	40.90	66.04	76.87	84.25	70.29	73.40	79.02	82.86
Ash	11.94	13.12	8.39	16.50	12.62	20.37	7.60	8.33	25.02	26.13	5.21	5.47
Moisture	9.01	--	49.19	--	38.07	--	8.75	--	4.24	--	4.64	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis												
Carbon	42.13	46.3	21.5	42.32	25.72	41.54	43.79	47.99	38.02	39.70	40.90	42.89
Hydrogen	4.9	5.39	2.55	5.02	2.97	4.79	6.05	6.63	5.53	5.78	5.69	5.97
Oxygen	31.39	34.5	18.17	35.77	19.94	32.21	33.61	36.84	26.09	27.24	41.61	43.62
Nitrogen	0.52	0.57	0.17	0.33	0.53	0.85	0.13	0.14	0.77	0.80	1.67	1.75
Sulfur	0.11	0.12	0.03	0.06	0.15	0.24	0.07	0.07	0.33	0.35	0.28	0.30
Ash	11.94	13.12	8.39	16.5	12.62	20.37	7.6	8.33	25.02	26.13	5.21	5.47
Moisture	9.01	--	49.19	--	38.07	--	8.75	--	4.24	--	4.64	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	7,203	7,916	3,764	7,408	4,341	7,009	8,152	8,934	6,396	6,679	7,480	7,867
Chlorine %	0.05	0.05	0.01	0.02	0.19	0.3						
Water Soluble Alkalis %												
Na_2O			0.008	0.015							0.214	0.224
K_2O			0.095	0.187							0.123	0.129
CaO												
Elemental Composition												
SiO_2		45.91		65.77		59.65		28.10		33.81		2.99
Al_2O_3		15.55		14.84		3.06		52.56		12.71		11.92
TiO_2		2.09		0.55		0.32		4.29		1.66		24.30
Fe_2O_3		12.02		5.27		1.97		0.81		5.47		19.55
CaO		13.51		5.78		23.75		7.49		23.44		12.38
MgO		2.55		1.81		2.15		2.36		5.64		1.38
Na_2O		1.13		2.70		1.00		0.53		1.19		3.58
K_2O		2.14		2.19		2.96		0.16		0.20		1.94
SO_3		2.45		0.36		2.44		1.70		2.63		9.30
P_2O_5		0.94		0.66		1.97		0.20		0.67		0.78
CO_2/other				0.45								1.27
Undetermined		1.71		-0.38		0.73		1.80		12.58		10.61
TOTAL		100.00		100.00		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu		0.54		1.09		1.15		0.06		0.54		0.38

Fuel	Willow		Willow		Willow		Willow		Willow		Willow		Willow		Willow	
Type	SV1-3Yr		SV1-1Yr		SP3-1Yr		SH3-1Yr		SA22-1Yr		SA22-3Yr		SA22-Top		SA22-Butt	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis																
Fixed Carbon	12.40	13.82	12.09	13.99	14.22	15.75	14.09	16.14	14.75	16.67	14.47	16.07	16.70	17.99	13.18	14.81
Volatile Matter	76.52	85.23	73.38	84.91	74.99	83.05	71.74	82.16	72.43	81.83	74.01	82.22	73.92	79.67	74.82	84.13
Ash	0.85	0.95	0.95	1.10	1.08	1.20	1.49	1.70	1.33	1.50	1.54	1.71	2.17	2.34	0.94	1.06
Moisture	10.23	--	13.58	--	9.71	--	12.68	--	11.49	--	9.98	--	7.21	--	11.06	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis																
Carbon	44.07	49.09	41.43	47.94	45.41	50.29	42.65	48.85	44.03	49.75	44.92	49.9	45.86	49.42	43.53	48.95
Hydrogen	5.29	5.89	5.05	5.84	5.43	6.01	5.27	6.04	5.31	6.00	5.31	5.9	5.47	5.89	5.38	6.05
Oxygen	39.21	43.69	38.39	44.43	37.85	41.93	37.24	42.64	37.18	42.01	37.63	41.81	38.28	41.27	38.73	43.54
Nitrogen	0.32	0.35	0.55	0.63	0.45	0.5	0.62	0.71	0.58	0.65	0.55	0.61	0.89	0.96	0.32	0.36
Sulfur	0.03	0.03	0.05	0.06	0.07	0.07	0.05	0.06	0.08	0.09	0.07	0.07	0.12	0.12	0.04	0.04
Ash	0.85	0.95	0.95	1.1	1.08	1.2	1.49	1.70	1.33	1.50	1.54	1.71	2.17	2.34	0.94	1.06
Moisture	10.23	--	13.58	--	9.71	--	12.68	--	11.49	--	9.98	--	7.21	--	11.06	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	7,478	8,330	7,194	8,325	7,848	8,691	7,373	8,443	7,485	8,457	7,583	8,424	7,896	8,510	7,405	8,326
Chlorine %	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Water Soluble Alkalis %																
Na_2O	0.021	0.023	0.010	0.012	0.022	0.024	0.011	0.013	0.004	0.004	0.007	0.007	0.066	0.071	0.010	0.011
K_2O	0.113	0.126	0.147	0.012	0.245	0.271	0.243	0.278	0.270	0.305	0.242	0.269	0.466	0.503	0.145	0.163
CaO																
Elemental Composition																
SiO_2		8.08		16.76		2.83		1.11		1.89		2.35		2.05		1.82
Al_2O_3		1.39		3.01		0.12		0.09		0.16		1.41		1.97		1.48
TiO_2		0.06		0.07		0.06		0.00		0.04		0.05		0.03		0.05
Fe_2O_3		0.84		0.85		0.42		0.21		0.30		0.73		0.35		0.49
CaO		45.62		34.83		36.51		40.48		32.00		41.20		34.18		44.68
MgO		1.16		2.46		1.54		3.04		7.67		2.47		2.98		2.16
Na_2O		2.47		3.05		1.97		0.77		0.65		0.94		2.67		0.86
K_2O		13.20		12.20		19.9		13.90		22.10		15.00		18.4		15.30
SO_3		1.15		1.70		1.94		1.70		3.09		1.83		2.92		2.33
P_2O_5		10.04		10.36		12.9		8.16		11.68		7.40		7.1		7.18
CO_2/other		13.67		17.58		19.85		27.10		17.65		18.24		22.64		18.34
Undetermined		2.32		-2.87		1.96		3.44		2.77		8.38		4.71		5.31
TOTAL		100.00		100.00		100.00		100.00		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu		0.18		0.20		0.30		0.30		0.40		0.32		0.58		0.21

Fuel	Sugar Cane		Bana Grass		Switchgrass		Switchgrass		Switchgrass	
Type	Bagasse, HI		HI, Immature		Summer-MM, MN		Dakota Leaf, MN		Columbus, OH	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis										
Fixed Carbon	10.70	11.95	15.93	16.68	12.47	14.37	13.14	15.03	12.93	14.34
Volatile Matter	76.72	85.61	70.13	73.44	71.93	82.94	71.07	81.36	69.14	76.69
Ash	2.19	2.44	9.43	9.88	2.33	2.69	3.15	3.61	8.09	8.97
Moisture	10.39	--	4.51	--	13.27	--	12.64	--	9.84	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis										
Carbon	43.59	48.64	43.02	45.06	41.21	47.51	41.45	47.45	42.09	46.68
Hydrogen	5.26	5.87	5.18	5.42	5.03	5.80	5.02	5.75	5.25	5.82
Oxygen	38.39	42.85	36.95	38.69	37.81	43.60	37.02	42.37	33.87	37.57
Nitrogen	0.14	0.16	0.80	0.84	0.31	0.36	0.65	0.74	0.69	0.77
Sulfur	0.04	0.04	0.11	0.11	0.04	0.04	0.07	0.08	0.17	0.19
Ash	2.19	2.44	9.43	9.88	2.33	2.69	3.15	3.61	8.09	8.97
Moisture	10.39	--	4.51	--	13.27	--	12.64	--	9.84	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	7,317	8,166	7,193	7,533	6,920	7,979	7,001	8,014	7,002	7,766
Chlorine %	0.03	0.03	0.79	0.83	<0.01	0.01	0.03	0.03	0.17	0.19
Water Soluble Alkalis %										
Na_2O			0.016	0.017	0.004	0.004	0.003	0.003		
K_2O			3.520	3.686	0.134	0.154	0.208	0.238		
CaO										
Elemental Composition										
SiO_2		46.61		33.65		61.64		61.23		65.18
Al_2O_3		17.69		0.80		1.32		0.57		4.51
TiO_2		2.63		0.07		0.19		0.37		0.24
Fe_2O_3		14.14		0.63		1.08		0.79		2.03
CaO		4.47		3.57		11.11		12.06		5.60
MgO		3.33		1.71		4.86		5.42		3.00
Na_2O		0.79		0.38		0.64		0.43		0.58
K_2O		4.15		42.80		8.24		7.63		11.60
SO_3		2.08		0.85		0.80		1.11		0.44
P_2O_5		2.72		2.74		3.09		3.56		4.50
CO_2/other				8.97						
Undetermined		1.39		3.83		7.03		6.83		2.32
TOTAL		100.00		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu		0.15		5.66		0.30		0.36		1.41

Appendix C.5 Grasses and Straws:
Tropical and Temperate Energy Crops

Fuel	Miscanthus		Sorghastrum		Miscanthus		Arundo	
Type	Silberfeder		Avenaceum		Sinensis Gracillimus		Arundo Bonax	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis								
Fixed Carbon	10.73	12.55	12.57	14.18	14.27	16.30	9.50	16.38
Volatile Matter	72.12	84.40	72.42	81.67	70.28	80.34	46.50	80.19
Ash	2.61	3.05	3.68	4.15	2.94	3.36	1.99	3.43
Moisture	14.54	--	11.33	--	12.51	--	42.01	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis								
Carbon	40.41	47.29	41.94	47.30	41.70	47.66	27.29	47.06
Hydrogen	4.92	5.75	5.33	6.01	5.03	5.75	3.39	5.84
Oxygen	37.19	43.52	37.40	42.18	37.39	42.73	24.9	42.95
Nitrogen	0.28	0.33	0.28	0.32	0.39	0.45	0.35	0.6
Sulfur	0.05	0.06	0.04	0.04	0.04	0.05	0.07	0.12
Ash	2.61	3.05	3.68	4.15	2.94	3.36	1.99	3.43
Moisture	14.54	--	11.33	--	12.51	--	42.01	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	6,879	8,050	7,131	8,042	7,131	8,150	4,700	8,104
Chlorine %	0.05	0.06	0.04	0.04	0.07	0.08	0.12	0.20
Water Soluble Alkalis %								
Na_2O	0.003	0.003	0.005	0.005	0.003	0.003	0.002	0.003
K_2O	0.288	0.337	0.295	0.332	0.545	0.623	0.649	1.118
CaO								
Elemental Composition								
SiO_2		61.84		71.05		56.07		44.21
Al_2O_3		0.98		1.78		0.78		0.80
TiO_2		0.05		0.02		0.02		0.10
Fe_2O_3		1.35		0.92		0.93		0.86
CaO		9.61		6.81		13.62		2.78
MgO		2.46		2.14		1.07		3.07
Na_2O		0.33		0.24		0.27		0.49
K_2O		11.60		8.70		18.70		30.00
SO_3		2.63		1.08		1.70		4.82
P_2O_5		4.20		4.30		6.24		6.16
CO_2/other								
Undetermined		4.95		2.96		0.60		6.71
TOTAL		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu		0.45		0.46		0.78		1.29

Fuel	Straws		Straws		Straws		Straws		Straws		Straws		Straws/Husks		Straws	
Type	Alfalfa Stems		Mint		Wheat DK		Wheat-OR		Wheat-CA		Wheat-Imperial		Rice Hulls		Rice	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis																
Fixed Carbon	14.34	15.81	16.16	19.42	12.29	14.87	15.38	17.06	16.47	17.71	16.82	19.34	14.44	16.22	14.60	15.86
Volatile Matter	71.59	78.92	58.05	69.80	67.09	81.24	70.84	78.62	69.97	75.27	61.86	71.11	56.57	63.52	60.28	65.47
Ash	4.78	5.27	8.97	10.78	3.21	3.89	3.89	4.32	6.52	7.02	8.31	9.55	18.05	20.26	17.19	18.67
Moisture	9.29	--	16.82	--	17.41	--	9.89	--	7.04	--	13.01	--	10.94	--	7.93	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis																
Carbon	42.79	47.17	37.61	45.22	39.27	47.55	42.32	46.96	41.75	44.92	37.32	42.90	34.58	38.83	35.20	38.24
Hydrogen	5.44	5.99	4.59	5.52	4.84	5.86	5.12	5.69	5.07	5.46	4.44	5.11	4.23	4.75	4.79	5.20
Oxygen	35.09	38.69	29.75	35.76	34.71	42.02	38.22	42.41	39.08	42.00	36.20	41.62	31.69	35.59	33.92	36.84
Nitrogen	2.43	2.68	2.05	2.47	0.48	0.59	0.39	0.43	0.40	0.44	0.46	0.53	0.46	0.52	0.80	0.87
Sulfur	0.18	0.2	0.21	0.25	0.08	0.09	0.17	0.19	0.14	0.16	0.26	0.29	0.05	0.05	0.17	0.18
Ash	4.78	5.27	8.97	10.78	3.21	3.89	3.89	4.32	6.52	7.02	8.31	9.55	18.05	20.26	17.19	18.67
Moisture	9.29	--	16.82	--	17.41	--	9.89	--	7.04	--	13.01	--	10.94	--	7.93	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	7,280	8,025	6,312	7,589	6,529	7,905	7,152	7,937	7,171	7,714	6,288	7,228	6,065	6,811	5,971	6,486
Chlorine %	0.45	0.50	0.35	0.43	0.14	0.17	0.13	0.14	0.21	0.23	1.79	2.06	0.11	0.12	0.54	0.58
Water Soluble Alkalis %																
Na_2O	0.109	0.120	0.081	0.097	0.057	0.069							0.019	0.022		
K_2O	1.050	1.158	2.580	3.102	0.301	0.365							0.592	0.665		
CaO														0.008		
Elemental Composition																
SiO_2		5.79		19.45		55.32		46.07		55.32		37.06		91.42		74.67
Al_2O_3		0.07		4.61		0.84		1.69		1.88		2.23		0.78		1.04
TiO_2		0.02		0.27		0.22		0.09		0.08		0.17		0.02		0.09
Fe_2O_3		0.30		2.33		1.05		1.85		0.73		0.84		0.14		0.85
CaO		18.32		14.60		12.27		9.95		6.14		4.91		3.21		3.01
MgO		10.38		5.71		2.48		2.45		1.06		2.55		<0.01		1.75
Na_2O		1.10		1.64		1.51		1.18		1.71		9.74		0.21		0.96
K_2O		28.10		26.50		12.9		25.20		25.60		21.70		3.71		12.30
SO_3		1.93		2.90		2.49		4.92		4.40		4.44		0.72		1.24
P_2O_5		7.64		4.78		4.3		3.32		1.26		2.04		0.43		1.41
CO_2/other		14.8		10.50												
Undetermined		11.55		6.71		6.62		3.28		1.82		14.32				2.68
TOTAL		100.00		100.00		100.00		100.00		100.00		100.00		100.64		100.00
Alkali, Lb/MMBtu		1.92		4.00		0.71		1.44		2.49		4.15		1.17		3.82

Fuel	Almond		Almond		Pistachio		Walnut		Walnut		Olive		Prune	
Type	Shells		Hulls		Shells		Blows		Hulls and Blows		Pits		Pits	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis														
Fixed Carbon	19.28	20.71	18.76	20.07	15.67	16.95	12.87	16.82	9.11	17.47	15.29	16.28	11.82	17.80
Volatile Matter	70.73	76.00	68.99	73.80	75.49	81.64	61.83	80.82	41.50	79.58	77.01	82.00	53.65	80.79
Ash	3.06	3.29	5.73	6.13	1.30	1.41	1.81	2.36	1.54	2.95	1.62	1.72	0.94	1.41
Moisture	6.93	--	6.52	--	7.54	--	23.49	--	47.85	--	6.08	--	33.59	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ultimate Analysis														
Carbon	45.88	49.3	44.43	47.53	46.42	50.20	41.05	53.65	27.90	53.51	49.59	52.80	32.71	49.26
Hydrogen	5.55	5.97	5.58	5.97	5.84	6.32	4.97	6.5	3.40	6.52	6.28	6.69	4.38	6.59
Oxygen	37.83	40.64	36.62	39.18	38.06	41.16	27.58	36.05	18.45	35.38	35.96	38.29	27.77	41.83
Nitrogen	0.71	0.76	1.06	1.13	0.64	0.69	1.02	1.34	0.80	1.53	0.42	0.45	0.56	0.84
Sulfur	0.04	0.04	0.06	0.06	0.20	0.22	0.08	0.1	0.06	0.11	0.05	0.05	0.05	0.07
Ash	3.06	3.29	5.73	6.13	1.30	1.41	1.81	2.36	1.54	2.95	1.62	1.72	0.94	1.41
Moisture	6.93	--	6.52	--	7.54	--	23.49	--	47.85	--	6.08	--	33.59	--
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, Btu/lb	7,797	8,378	7,590	8,119	8,469	7,831	7,345	9,600	4,976	9,541	8,718	9,282	5,737	8,638
Chlorine %	<0.01	<0.01	0.02	0.02	<0.01	<0.01	0.02	0.02	0.01	0.02	0.04	0.04	<0.01	<0.01
Water Soluble Alkalis %														
Na_2O														
K_2O														
CaO														
Elemental Composition														
SiO_2		8.71		9.28		8.22		5.18		6.88		30.82		3.00
Al_2O_3		2.72		2.09		2.17		1.82		2.42		8.84		0.09
TiO_2		0.09		0.05		0.20		0.09		0.09		0.34		0.02
Fe_2O_3		2.30		0.76		35.37		0.85		1.14		6.58		0.57
CaO		10.50		8.07		10.01		22.32		16.62		14.66		12.25
MgO		3.19		3.31		3.26		11.58		13.45		4.24		9.72
Na_2O		1.60		0.87		4.50		0.74		0.99		27.80		0.39
K_2O		48.70		52.90		18.20		28		32.90		4.40		37.50
SO_3		0.88		0.34		3.79		1.88		2.25		0.56		2.07
P_2O_5		4.46		5.10		11.80		8.3		6.24		2.46		16.80
CO_2/other		17.38		20.12										
Undetermined		-0.53		-2.89		2.48		19.24		17.02		-0.70		17.59
TOTAL		100.00		100.00		100.00		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu		1.98		4.06		0.41		0.71		1.05		0.60		0.62

APPENDIX D: DEPOSITS

D1. Melting Temperature of Potential Low-Melting Minerals Found in Biomass

D.2 Grate - 1. Fuels and Deposits firing Wood and Wood/Straw (5% Imperial Wheat Straw)

D.3 Grate-1. Fuels and Deposits from firing 80% Wood with 20% Oregon Wheat straw.

D.4 A Northeastern boiler similar to Grate-1 with severe slagging. Fireside deposits diminished when landscape fuel was removed.

D.5 Danish straw-fired Grate-2 and Grate 3. Low temperature boiler.

D.6 FBC-1 firing wood with agricultural prunings.

D.7 CFB-1 and CFB-2 firing different blends of wood and agricultural residues.

D.8 CFB-3 firing high concentration of pits and hulls with wood fuels.

Appendix D.1
Melting Temperature of Potential Low-Melting Minerals Found in Biomass*

Group	Mineral	Melting Temperature, °C
Chlorides	NaCl	801
	$CaCl_2$	782
	KCl	770
	$MgCl_2$	714
	$FeCl_3$	306
Carbonates	Na_2CO_3	851
	$CaCO_3$	1339
	K_2CO_3	891
	$MgCO_3$	Decomp. 350
	$FeCO_3$	Decomp. 350
Chlorates	$NaClO_3$	248-261
	$Ca(ClO_3)_2$	340
	$KClO_3$	356, decomp. 400
	$MgClO_3 \cdot 6H_2O$	35
	Iron $Fe(ClO_4)_2$	Decomp. >400
Sulfates	Na_2SO_4	--
	$CaSO_4$	750-950 (pres. of silicates)
	K_2SO_4	1069 Tr. 558
	$MgSO_4$	1124 Decomp.
	$Fe(SO_4)_3$	480 Decomp.
Hydroxides	Na(OH)	318
	$Ca(OH)_2$	580—H_2O
	KOH	360
	Mg(OH)	350—H_2O
	$Fe(OH)_2$	--
Sulfides	Na_2S	1180
	K_2S	470
	MgS	--
	FeS_2	1171
Phosphates	$Ca_2P_2O_7$	1230
	K_3PO_4	1340
	$Mg_3(PH_4)_2$	1184

*Ref.: R.W. Bryers, 1994. Analysis of A Suite of Biomass Fuels, FOSTER WHEELER DEVELOPMENT CORPORATION, FWC/FWDC/TR-94/03, May 6. 1994, Table 8.

Plant	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1
Location		Abv Feeder	South Wall	Superheater	Superheater	Fuel Pile	Straw pile	Conveyor	Grate	Preheat
Form	fuel	sintered	deposits	wedge	Flyash	fuel ash	fuel ash	fuel ash	clinker	flyash
	Average	DEP007	DEP010	DEP002	STR6-9					
Analysis		D194/93-5	D194/93-3	D194/93-1	C500-93-4	A139/93-1	A139/93-2	A139/93-3-7	A139/93-11	A139/93-9
Date		4/16/93	4/16/93	4/16/93	4/16/93	1/13/93	1/1/93	1/13/93	1/13/93	1/13/93
Fuel	wood	wood	wood	wood	wood	wood	straw	5% straw	5% straw	5% straw
	1	2	3	4	5	1	2	3	4	5
Elemental Composition										
SiO_2	55.24	60.79	59.67	31.57	62.38	53.24	37.02	51.74	60.47	60.42
Al_2O_3	11.91	12.50	13.13	8.53	12.07	11.57	2.23	11.02	11.44	10.52
TiO_2	0.73	0.74	0.74	0.50	0.72	0.56	0.17	1.03	0.60	0.60
Fe_2O_3	5.87	4.06	4.32	3.71	3.85	8.15	0.82	5.57	2.67	4.21
CaO	12.95	12.48	12.47	19.26	11.50	13.41	4.91	14.45	9.73	8.81
MgO	2.86	3.08	2.92	4.16	2.63	3.06	2.55	3.42	2.56	2.55
Na_2O	3.13	2.75	2.78	4.29	2.64	2.95	9.74	3.94	3.67	3.65
K_2O	4.63	3.80	3.52	9.10	3.67	3.23	21.70	5.00	5.19	5.07
SO_3	1.75	0.07	0.13	12.00	0.36	1.13	4.44	1.72	0.78	0.84
P_2O_5	0.97	1.14	1.58	1.34	1.10	0.89	2.04	1.27	0.92	0.87
CO_2										
Undetermined	-0.04	-1.41	-1.26	5.54	-0.92	1.81	14.38	0.84	1.97	2.46
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash %	6.60					4.89	8.12	3.35		
Chlorine %										
Chlorine in Fuel	0.09					0.03	1.75	0.10		
Chlorine in Ash	1.36	<0.01	<0.01	1.75	0.29	0.61	21.55	2.99		
X-ray Diffraction										
Primary - 40 to 100%										
Secondary - 20 to 60%									Leucite - $KAlSi_2O_6$	
									Quartz - SiO_2	
Minor - 5 to 30%									Anorthite - $(Ca,Na)(Si,Al)_4O_8$	
Trace - 1 to 10%									Gehlenite - $CaAl_2SiO_7$	
SEM									Yes	

Plant	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1	Grate-1
Location	Conveyor	South Wall	SW Str Level	Superheater	Superheater	Hopper	Gas Stream
Form	Fuel	Deposit	Chalk	Wedge	Flyash	Preheater	Preheater
Analysis Date Fuel	Average 80% wood 20% straw	DEP 011 D194/93-9 4/16/93 wood/straw	DEP 007 D194/93-8 4/16/93 wood/straw	DEP 008 D194/93-10 4/16/93 wood/straw	STR1-5 C500/93-12 4/16/93 wood/straw	DEP 008 C500/93-10 4/16/93 wood/straw	DEP 008a C551/93-2 4/16/93 wood/straw
	1	2	3	4	5	6	7
Elemental Composition							
SiO_2	57.58	55.44	5.41	33.70	61.98	62.19	55.90
Al_2O_3	10.16	10.61	1.63	9.47	9.99	12.06	10.39
TiO_2	0.48	0.82	0.07	0.50	0.51	0.58	0.49
Fe_2O_3	3.98	4.07	2.74	3.57	3.27	3.71	3.43
CaO	11.29	11.67	4.97	14.68	10.13	10.48	11.18
MgO	2.96	2.86	1.26	3.79	2.46	2.79	2.88
Na_2O	3.04	2.77	9.05	4.09	2.41	2.49	2.92
K_2O	6.89	6.86	27.90	11.80	7.82	5.60	8.44
SO_3	2.26	2.99	41.90	16.30	1.46	0.35	2.02
P_2O_5	1.07	1.05	0.76	1.12	1.19	1.26	1.15
CO_2							
Undetermined	0.29	0.86	4.31	0.98	-1.22	-1.51	1.20
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash %	6.68						
Chlorine %							
Chlorine in Fuel	0.16						
Chlorine in Ash	2.24	0.19	0.21	0.29	0.1		
X-ray Diffraction							
Primary - 40 to 100%			Aphthitalite - $K_3Na(SO_4)_2$				
Secondary - 20 to 60%				$KNaSO_4$,Unident			
Minor - 5 to 30%			Palmierite - $K_2Pb(SO_4)_2$	Quartz - SiO_2 $K_2Ca_2(SO_4)_3$			
Trace - 1 to 10%				Albite-$NaAlSi_3O_8$ Angite- $Ca(MgFe)Si_2O_6$			
SEM				Yes			

Appendix D.3 Grate-1. Fuels and Deposits from firing 80% Wood with 20% Oregon Wheat straw.

Plant	Grate-1Type, Northeast, USA											
Fuel	Fuel		Wood		Wood		Slag Sample		Glassy Slag		Deposit	
Type	Specification		Main Fuel Pile		Landscape		Firebox		Firebox		Generating Tubes	
	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry	As Rec'd	Dry
Proximate Analysis												
Combustible	53.02	96.40	51.38	83.99	30.17	63.73						
Ash	1.98	3.60	9.08	16.01	17.17	36.27						
Moisture	45.00	--	39.54	--	52.66	--						
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00						
Ultimate Analysis												
Carbon	29.31	53.29										
Hydrogen	2.96	5.38										
Oxygen	20.64	37.52										
Nitrogen	0.07	0.13										
Sulfur	0.02	0.04	0.06	0.09	0.02	0.04						
Ash	2.00	3.64	9.08	16.01	17.17	36.27						
Moisture	45.00	--	39.54	--	52.66	--						
Undetermined			51.32	83.90	30.15	63.69						
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00						
HHV, Btu/lb	4,730	8,600	4,427	7,323	2,674	5,649						
Chlorine %							0.17	0.17	0.10	0.10	2.71	2.71
Elemental Composition												
SiO_2				47.07		67.65		60.13		66.03		35.23
Al_2O_3				6.88		11.44		8.89		9.84		7.86
TiO_2				0.39		0.74		0.50		0.50		0.41
Fe_2O_3				3.21		4.60		3.97		3.93		3.12
CaO				21.41		5.74		15.35		11.25		20.78
MgO				2.00		0.76		3.07		3.05		4.16
Na_2O				0.70		2.03		2.30		2.28		4.87
K_2O				2.87		3.44		3.29		2.64		6.94
SO_3				2.84		0.41		0.11		0.06		8.45
P_2O_5				1.09		0.17		1.13		0.93		1.76
CO_2												
Undetermined				11.54		3.02		1.26		-0.51		6.42
TOTAL				100.00		100.00		100.00		100.00		100.00
Alkali, Lb/MMBtu				0.78		3.51						

Appendix D.4 A Northeastern boiler similar to Grate-1 with severe slagging.

Plant	Grate-2	Grate-2	Grate-2	Grate-2	Grate-2	Grate-3	Grate-3	Grate-3	Grate-3	Grate-3	Grate-3
Location		Grate	Superhtr	Sec Shtr	Dust	Nozzle	Nosewall	Wall	Wall	FurnExit	Sec Shtr
Form	Fuel	slag	chalk	w/oFe$_2$O$_3$	Collect	sintered	deposits	deposits	deposits	deposits	deposits
	Average										
Analysis	K176/93	K177/93-2	K177/93-1	K177/93-3	K177/93-4	K177/93-5	K177/93-6	K177/93-7	K177/93-8	K177/93-9	K177/93-1
Date	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93	11/8/93
Fuel	straw	straw	straw	straw	straw	straw	straw	straw	straw	straw	straw
	1	2	3	4	5	2	3	4	5	6	7
Elemental Composition											
SiO$_2$	63.42	62.26	18.62	20.93	8.64	49.51	48.92	40.22	7.54	43.83	10.64
Al$_2$O$_3$	1.95	1.94	1.12	4.20	1.41	2.16	12.15	1.02	1.55	0.89	0.99
TiO$_2$	0.02	0.07	0.02	0.03	0.02	0.05	0.09	0.02	0.02	0.05	0.02
Fe$_2$O$_3$	0.66	0.48	0.32		2.80	0.66	0.55	0.38	0.52	0.46	8.73
CaO	4.20	10.59	14.41	16.45	5.82	15.09	10.93	11.30	3.79	11.79	4.80
MgO	0.46	2.15	2.45	1.38	0.56	2.71	0.64	2.30	0.08	2.53	0.80
Na$_2$O	0.83	0.47	0.47	1.31	0.79	1.58	0.92	1.29	1.12	1.28	0.97
K$_2$O	13.10	17.70	33.4	40.13	49.81	18.70	19.7	25.10	51.2	22.4	43.50
SO$_3$	1.95	0.04	8.67	10.90	8.86	0.20	0.98	4.94	5.99	6.91	3.90
P$_2$O$_5$	4.96	3.74	3.46	5.41	2.12	3.94	2.87	2.58	1.06	3.07	1.29
CO$_2$		0.12	0.3	0.44	0.64	0.06	0.05	0.11	0.16	5	0.05
Undetermined	8.45	0.44	16.76	-1.17	18.53	5.34	2.2	10.74	26.97	1.79	24.31
TOTAL	100.00	100.00	100.00	100.01	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash %	6.68										
Chlorine %											
Chlorine in Fuel	0.16										
Chlorine in Ash	3.4	0.04	15.2	22.85	21.8	4.89	0.28	6.81	29.2	1.42	26
SEM					Yes						

Appendix D.6 FBC-1 firing wood with agricultural prunings.

Plant	FBC-1	FBC-1	FBC-1	FBC-1	FBC-1
Location	Fuel	Furn Wall	Scr Tubes	Tertiary	Sec Str
Form	ash	deposit	wedge	wedge-top	wedge
Analysis Date Fuel	Average wood/ag	DEL-17 K311/93-13 11/24/93 wood/ag	DEL-5 K311/93-4 11/24/93 wood/ag	DEL-13 K311/93-10 11/24/93 wood/ag	DEL-8 K311/93-6 11/24/93 wood/ag
	1	2	3	4	5
Elemental Composition					
SiO_2	28.27	62.76	10.27	8.97	16.78
Al_2O_3	8.28	11.49	4.62	3.16	5.53
TiO_2	0.84	0.53	0.40	0.27	0.59
Fe_2O_3	3.33	2.94	1.69	4.29	2.48
CaO	28.99	10.15	27.71	19.34	27.95
MgO	4.51	1.40	6.64	2.03	3.27
Na_2O	2.81	2.26	2.04	3.14	2.68
K_2O	9.58	4.72	13.40	25.90	13.90
SO_3	2.14	0.36	26.70	17.90	13.10
P_2O_5	2.95	0.74	2.48	1.40	2.40
CO_2	4.98	0.26	1.58	2.33	4.10
Undetermined	3.32	2.39	2.47	11.27	7.22
TOTAL	100.00	100.00	100.00	100.00	100.00
Ash %	2.3				
Chlorine %					
Chlorine in Fuel	0.04				
Chlorine in Ash	1.74	0.13	3.26	14.20	7.37
X-ray Diffraction					
Primary - 40 to 100%				Sylvite - KCl	
Secondary - 20 to 60%		Leucite - $KAlSi_2O_6$ Quartz - SiO_2 Anorthite - $(Ca,Na)(Si,Al)_4O_8$			
Minor - 5 to 30%				$K_2Ca_2(SO_4)_3$	
Trace - 1 to 10%		Unident		NaCl Calcite -$CaCO_3$ Quartz - SiO_2 $Ca_{10}(SiO_4)_3(SO_4)(OH)_2$	
Amorphous halo?		No		No	
SEM		Yes		Yes	

Plant	CFB-1	CFB-1	CFB-1	CFB-1	CFB-1	CFB-2	CFB-2	CFB-2	CFB-2
Location	Tert Str	Tert Str	Sec Str	Pri Str	Superheater		Tert Str	Sec Str	Air Heater
Form	wedge-top	wedge	wedge	wedge	wedge	Fuel	wedge	wedge	flyash
Analysis	WLD-DEP-1	WLD-DEP-2	WLD-DEP-4	WLD-DEP-5	WLD-DEP-6	Average	Mendota 1	Mendota 4	Mendota 16
	K314/93-1	K314/93-2	K314/93-4	K314/93-5	K314/93-6		E209/93-1	E209/93-4	E209/93-16
Date	11/26/93	11/26/93	11/26/93	11/26/93	11/26/93		5/18/93	5/18/93	5/18/93
Fuel	wood-ag	wood-ag	wood-ag	wood-ag	wood-ag	wood/almond	wood/almond	wood/almond	wood/almond
	1	2	3	4	5	1	2	3	4
Elemental Composition									
SiO_2	12.80	13.30	11.78	13.88	12.47	48.35	9.05	12.01	45.58
Al_2O_3	6.15	6.60	6.52	6.63	4.92	11.11	2.78	4.42	9.60
TiO_2	0.56	0.62	0.51	0.58	0.46	0.51	0.28	0.36	0.31
Fe_2O_3	3.89	4.19	4.14	4.29	3.80	4.17	1.74	2.27	12.18
CaO	25.50	28.18	23.28	22.84	18.17	17.48	34.90	38.99	9.77
MgO	5.96	6.86	6.66	6.10	4.82	3.77	8.65	5.89	1.59
Na_2O	3.32	2.86	4.53	4.44	5.05	2.56	0.80	1.18	1.87
K_2O	9.41	7.76	9.99	9.31	13.40	6.90	5.70	7.01	4.04
SO_3	29.70	26.30	28.1	26.40	30.90	1.38	23.80	25.10	3.04
P_2O_5	2.65	3.09	2.76	2.78	2.40	1.49	2.25	2.42	0.84
CO_2	0.15	0.09	0.11	0.17	0.23		9.58		
Undetermined	-0.09	0.15	1.62	2.58	3.38	2.28	0.47	0.35	11.18
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash%						6.28			
Chlorine %									
Chlorine in Fuel						0.02			
Chlorine in Ash	0.01	0.01	0.21	0.47	1.11	0.32	0.22	0.33	0.26

X-ray Diffraction	Outer - WLD-1	Inner - WLD-1			
Primary - 40to 100%	$K_2Ca_2(SiO_4)_3$	$Ca_2MgSi_2O_7$			
		$Ca_2Al_2SiO_7$			
Secondary - 20 to 60%	Monticellite				
	$CaMgSiO_4$				
Minor - 5 to 30%	$Ca_5(PO_4)_3(OH)$	$Ca_5(PO_4)OH$			
	Fe_3O_4	$Ca_3Fe_2SiO_{12}$			
		$CaMgSiO_4$			
		$K_2Ca_2(SO_4)_3$			
		Unidentified			
Trace - 1 to 10%	Unidentified				
Amorphous halo?	No	No			
SEM	Yes	Yes			

Plant	CFB-3	CFB-3	CFB-3	CFB-3	CFB-3
Location	Fuel	U-Beam	UB Door	1st Sec	Finish Secondary
Form		deposit	powder	deposit	deposit
Analysis	Average	K309/93-1	K309/93-2	K309/93-3	K309/93-4
Date		11/23/93	11/23/93	11/23/93	11/23/93
Fuel	wood/pit	wood/pit	wood/pit	wood/pit	wood/pit
	1	2	3	4	5
Elemental Composition					
SiO_2	52.55	50.27	70.58	65.06	20.17
Al_2O_3	13.15	15.05	14.67	16.28	9.02
TiO_2	0.43	0.62	0.64	0.88	0.55
Fe_2O_3	8.18	3.78	4.93	6.46	6.45
CaO	10.06	13.21	4.31	5.38	26.29
MgO	3.27	2.49	1.24	1.70	4.65
Na_2O	5.90	3.21	1.62	2.00	2.47
K_2O	5.04	10.00	1.56	1.80	6.31
SO_3	2.10	0.02	0.03	0.74	20.30
P_2O_5	1.90	1.23	0.22	0.36	2.16
CO_2					
Undetermined	-2.58	0.12	.0.2	-0.66	1.63
TOTAL	100.00	100.00	100.00	100.00	100.00
Ash %	5.13				
Chlorine %					
Chlorine in Fuel	0.03				
Chlorine in Ash	0.58	0.03	<0.01	<0.01	0.05
X-ray Diffraction					
Primary - 40 to 100%					Anhydrite - $CaSO_4$
Secondary - 20 to 60%		Diopside - $CaO.MgO.2SiO_2$ Wollastonite - $CaO.SiO_2$ w/MgO			
Minor - 5 to 30%		Orthoclase - $KAlSi_3O_8$			$K_2Ca_2(SO_4)_3$
Trace - 1 to 10%		Unidentified			hydroxylapatite - $Ca_5(PO_4)_3OH$ monticellite $CaMgSiO_4$, UND
Amorphous halo?		No			No
SEM		Yes			Yes

Appendix D.8 CFB-3 firing high concentration of pits and hulls with wood fuels.